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Evaluation of Sampling and Sample Preparation Modifications for Soil Containing Metallic Residues

ER-0918

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Abstract:

Research over the last decade has revealed that releases of energetic constituents into the environment as a result of military training occur in extremely heterogeneous patterns. Traditional soil sampling and sample preparation methodologies are inadequate to address the level of contaminant heterogeneity observed. Consequently, research conducted identified a number of necessary changes to the accepted soil sampling and sample preparation procedures, which were adopted in a revised U.S. Environmental Protection Agency (USEPA) Method 8330B. Recently, there have been questions regarding whether the issues observed for the deposition of energetic constituents also substantively apply to other constituents such as metals, semi-volatile organic compounds, and polychlorinated biphenyls. Preliminary data suggest metal constituents introduced into the environment as metal residues from small arms and pyrotechnic military training are heterogeneously distributed. As a result of these findings regulatory agencies are increasingly requiring the DOD to apply procedures developed for energetics under USEPA Method 8330B to the sampling and sample processing of soil samples from small arms ranges containing metals. However, there is no published research indicating whether changes to USEPA Method 3050B for metals are needed or warranted. This study assessed the procedures developed and adopted for energetics using USEPA Method 8330B and whether they are applicable to soils containing metals. The utility of multi-increment sampling versus traditional grab/discrete sampling was assessed and found to yield reproducible and more representative metals soil concentrations. In addition, changes to the soil digestion procedure, USEPA Method 3050B, were evaluated and included the following: 1) necessity of machining/grinding of the soil, appropriate type of grinding apparatus, and grinding interval; 2) assessment of the need to increase the digested mass and digestion interval; 3) optimum soil to acid ratio, i.e. digestion efficiency; 4) sub sampling to build the digestate sample; and 5) disposition of the oversize fraction, i.e. material larger than 2-mm. larger than 2-mm.

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Nomenclature

BRAC	Base Realignment and Closure
COC	contaminant of concern
CRREL	Cold Regions Research and Engineering Laboratory
CMIST	CRREL Multi-Increment Sampling Tool
CSM	Conceptual site model
DOD	Department of Defense
DI	De-ionized water
DQO	Data quality objectives
DU	Decision unit
EL	Environmental Laboratory
FE	Fundamental Error
FUDS	Formerly Used Defense Sites
ICP-OES	Inductively coupled plasma – optical emission spectrometry
IQRs	Interquartile ranges
KW	Kruskal-Wallis test
MI	Multi-increment
MMRP	Military Munition Response Program
RSD	Relative standard deviation
SI	Site Investigation
UCL	Upper confidence limit
USACE	U.S. Army Corps of Engineers
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
UXO	Unexploded ordnance

Preface

This study was conducted for the Environmental Science and Technology Certification Program under Project ER-0918, *Demonstration of the Attributes of Multi-Increment Sampling and Proper Sample Processing Protocols for the Characterization of Metals on DoD Facilities*. The technical monitor was A. Leeson.

The work was performed by the Biogeochemical Science Branch (BSB) of the Research and Engineering Division, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory (ERDC-CRREL). At the time of publication, Dr. T. Sobecki was Branch Chief, CEERD-RN, and Dr. J. Berman was Division Chief, CEERD-RN. The Deputy Director of ERDC-CRREL was Dr. Lance Hansen and the Director was Dr. Bert Davis.

COL Kevin J. Wilson was the Commander and Executive Director of ERDC, and Dr. Jeffery P. Holland was the Director.

Unit Conversion Factors

Multiply	By	To Obtain
acres	4,046.873	square meters (m ²)
cubic feet (ft ³)	0.02831685	cubic meters (m ³)
cubic inches (in ³)	1.6387064×10 ⁻⁵	cubic meters (m ³)
degrees Fahrenheit (°F) – 32	1/1.8	degrees Celsius (°C)
feet (ft)	0.3048	meters (m)
inches (in)	0.0254	meters (m)
microns (μm)	10 ⁻⁶	meters (m)
miles (U.S. statute) (mi)	1,609.347	meters (m)
mils	0.0254	millimeters (mm)
pounds (mass) (lb)	0.45359237	kilograms (kg)
square feet (ft ²)	0.09290304	square meters (m ²)
square inches (in ²)	6.4516×10 ⁻⁴	square meters(m ²)

1 Introduction

The U.S Army's Military Munitions Response Program (MMRP) was established under the Defense Environmental Restoration Program in 2001 to manage the environmental and health and safety issues associated with unexploded ordnance (UXO), discarded military munitions, and munitions constituents on non-operational ranges in active installations, Defense Base Realignment and Closure (BRAC) sites, and Formerly Used Defense Sites (FUDS). Under the MMRP, the Department of Defense (DoD) is required to: 1) inventory non-operational ranges that contain or are suspected to contain munitions-related material released before September 2002; 2) identify, characterize, track, and report data on MMRP sites and clean-up activities; and 3) develop a process to prioritize site cleanup and estimate costs. The Army completed their inventory of non-operational ranges in 2003 and began Site Investigations (SI) for these MMRP sites. Based on the SI findings, some ranges may require additional assessment under the Remedial Investigation process. In addition, established directives mandate all active DoD facilities implement procedures to assess environmental impacts from munitions on training and testing ranges (DoD Directive 4715.11 and DoD Instruction 4715.14).

Environmental studies of military training ranges have shown that energetic residues are heterogeneously distributed. To representatively sample military ranges where energetic residues have been introduced into the environment multi-increment (MI) sampling strategies are recommended (Hewitt et al. 2009). There is growing acceptance of incremental sampling and associated sample processing procedures for energetics by the environmental regulatory community (Hewitt et al. in press; ITRC 2011; Alaska 2009; Hawaii 2008). These changes are described in USEPA Method 8330B (USEPA 2006).

Because of the success of the MI sampling for energetics, members of the environmental community are considering its adoption for other hazardous particulate constituents such as metals (Hewitt et al. in press; ITRC 2011; Alaska 2009; Hawaii 2008). The approach is frequently used for SIs conducted under Formerly Used Defense Sites (FUDS). Several state and federal agencies now prefer MI sampling designs. These currently include the states of Alaska, Hawaii, Ohio, and the U.S Environmental Protection

Agency (USEPA) Region 6. For example, the *Technical Guidance Manual for the Implementation of the Hawaii State Contingency Plan* states:

The HEER [Hazardous Evaluation and Emergency Response] Office strongly encourages the use of Multi-increment sample collection strategies to enhance sample representativeness in the investigation of contaminated soil.

Similarly, the *Draft Guidance on Multi Incremental Soil Sampling* from the State of Alaska Department of Environmental Conservation states:

An MI approach, if systematically planned and implemented, can accurately determine an average concentration representative of the soil contained within a defined area, i.e. the “decision unit”... DEC initially encourage the use of MI at sites where soil is contaminated with petroleum hydrocarbons only. However, MI sampling may be applicable to contaminated sites with non-petroleum related contaminants...

The *Technical Guidance Compendium* from Ohio State EPA states:

With the inclusion of the MI sampling technique, an investigator can use a rigorous form of composite sampling to obtain a representative concentration for a chemical of concern (COC) without selecting the maximum concentration. If the site decision unit is represented by a single MI sample, the MI sample provides an estimate of central tendency concentrations and thus may eliminate the need for further statistical analysis of the data such as calculating the 95% UCL of the mean.

The current USEPA method for metals in soils is Method 3050B (USEPA 1996a). However, there is an absence of data demonstrating modifications to field sampling protocols and USEPA Method 3050B are warranted for analysis of soils containing metal residues. The working hypothesis is that the current field sampling and sample processing procedures for metals in soil do not yield representative and reproducible results for military sites where the metal is heterogeneously introduced into the environment as a solid residue.

2 Background

The development of MI methodology began with the realization in the mid 1990s that energetic residues were heterogeneously distributed and that the current sampling methodologies did not address this issue. Studies conducted in the early 2000s (Table 1) resulted in the development of a modified sample collection and processing methodology for energetic constituents. Anthropogenic metals are also heterogeneously distributed over active training ranges as particles of various sizes, shapes, and compositions (Fig. 1). To address the compositional and distributional heterogeneity (e.g., to obtain a representative and reproducible estimate of the mean concentration), the sampling strategy must acquire an adequate number of particles of the constituents of interest and these particles must be present in the sample in roughly the sample proportion as the Decision Unit (DU). The MI methodology is not limited to the laboratory sample processing; it also includes field sampling procedures and project planning (Table 2).

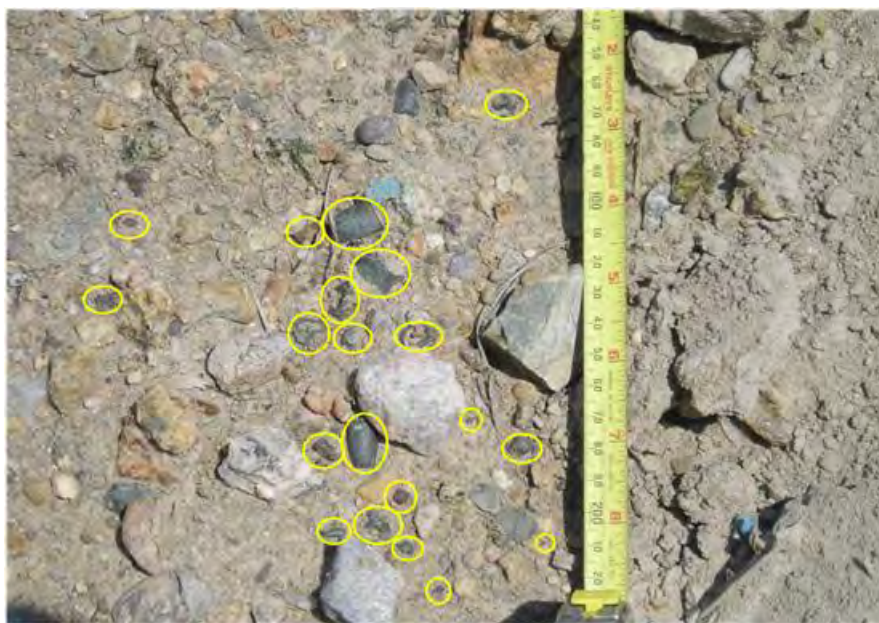


Figure 1. Visible small arms metal debris (yellow circles) found on a small arms range at Camp Edwards, Massachusetts.

Table 1. Chronological summary of multi-increment sampling.

Time Period	Activity	References
1960s–1990s	Recognition of the role of heterogeneity in distribution of metals in mining samples and development of methods to obtain representative samples	Duncan 1962, Johanson 1978 Elder et al. 1980 Gy 1982, 1999 Wallace et al. 1985 Pitard 1993 Leutwyler 1993, Studt 1995
Early 1990s–2004	Demonstration of presence of energetic residues on ranges	Racine et al. 1992 Jenkins et al. 1997a, b, 1998, 2001 Walsh and Collins 1993, Walsh et al. 1997 Thiboutot et al. 1998, 2000a, b, 2003 Ampleman et al. 2003a, b Clausen et al. 2004 Pennington et al. 2004 Taylor et al. 2004
1990s	Recognition of heterogeneity issues associated with environmental samples	Pitard 1993
Mid 1990s–Early 2000s	Recognition of heterogeneity issues for energetic constituents on military ranges	Racine et al. 1992 Jenkins et al. 1997a, b, 1999, 2000 Taylor et al. 2004 Walsh et al. 1993b, 1997
2001–2009	Development of sampling and sample processing methods for soils containing energetic constituents	Jenkins et al. 2001, 2004a,b, 2005,a 2006 Thiboutot et al. 2002 M. E. Walsh et al. 2002, 2003, 2005, 2006a, b Hewitt and M. E. Walsh 2003 Hewitt et al. 2005, 2007, 2009
2004–2007	Demonstration and comparison of multi-increment methodology with traditional grab sampling approach for soils with energetic constituents	Jenkins et al. 2004 M. E. Walsh et al. 2004 Hewitt et al. 2005 Nieman 2007
2007–2010	Demonstration of heterogeneous distribution of metals in soils from military ranges	Clausen et al. 2007, 2010 Clausen and Korte 2009a, b
2008–present	Adoption of multi-increment methodology for soils with metals	Hawaii 2008, Alaska 2009. ITRC 2011
2009–present	ESTCP ER-0918 Project	

Table 2. Schematic diagram of the multi-increment sampling methodology.

Project Stage	Specific Activity		
Project Planning	Conceptual Site Model		
	Determination of Investigation Objectives		
	Identification of Data Needs		
	Decision Unit Identification		
	Determination of Sample Depth Interval		
	Number of Increments per Sample		
Field Implementation	Sample Tool Selection		
	Collection of Soil Sample		
Sample Processing	Air Drying		
	Sieving		
	Particle Size Reduction (Grinding)		
	< 2 mm (examined)		> 2 mm (archived)
	Splitting (if necessary)		
	Subsampling		
	Metals Digestion	Energetics Extraction	
	Digestion Mass		
	Acid Mixtures		
	Soil to Solution Ratios		
Analysis	ICP-MS or ICP-OES	HPLC	

The first component of the MI sampling methodology involves project planning to determine the 1) conceptual site model (CSM), 2) project's objectives, 3) data needs, 4) DU configuration, 5) sampling depth, and 6) number of increments per sample. The soil samples from DUs should be physically collected only after the planning phase has been completed.

In the field, the first step is to define the boundaries of the DU with markers (typically flags or stakes). Then, the next step is to determine the approximate spacing between increments (e.g., if they are collected using systematic random sampling) and the number of rows of increments needed to achieve the total number of increments for each MI sample. For materials distributed non-uniformly, this results in a sample of considerable mass (i.e., > 1 kg) composed of 30 or more increments from evenly spaced locations throughout the DU (Fig. 2). Traditionally, the analysis of metals in the environment has relied on much smaller samples. A "grab" or individual discrete sample of several hundred grams is typically collected in a 4-oz amber glass jar, from which only a small portion is removed; a 1-2 g aliquot is often scooped from the top of the jar for extraction (acid digestion) by Method 3050B or Method 3051A (USEPA 1996a,b). To reduce the influence of compositional and distributional heterogeneity when estimating the mean concentration of an analyte within a DU, Method

8330B recommends collecting 30 or more evenly spaced increments to build a sample with a total sample mass of >1 kg (Jenkins et al. 2004a,b, 2005a, 2006; Walsh et al. 2005; Hewitt et al. 2005, 2007). The objective of this sampling technique is to obtain a representative portion of every particle size, composition (antimony, copper, lead, zinc, etc.), and configuration (e.g., spheres or elongated particles), and to avoid over- or under-sampling any portion of the DU.

Currently, if metal particles of as large as only 2 mm are present in the media being sampled, a large amount of uncertainty would be anticipated. This is based on the equation used to estimate the fundamental error (FE) (eq. 1, Pitard 1993).

$$FE^2 = \frac{Cd^3}{m_s} \quad (1)$$

where:

FE = Fundamental Error (relative variance)

C = constant (g/mm³)

d = diameter of largest particle (mm)

m_s = mass of sample (g)

With an approximate value of 20 for C , for a maximum particle diameter (d) of 1.95 mm and subsample mass (m_s) of 2.0 g, the FE is about 30%. This constitutes an estimate of the smallest possible uncertainty introduced by the laboratory's sub-sampling procedure and accounts for only compositional heterogeneity; it does not take into account the additional uncertainty from distributional heterogeneity within the DU and sample preparation errors. Depending on the data quality objectives (DQOs), a minimum uncertainty of 30% may be unacceptably large. To estimate the total uncertainty (e.g., for estimating mean concentrations of munitions constituents), replicate MI samples must be collected within the same DU. If this step is not included in a sampling plan, the total uncertainty of the DU mean cannot be determined.

2.1 Energetics residue deposition

Projectiles fired into an impact area undergoing explosive detonations as designed are called "high-order" detonations. When a round detonates, but malfunctions, and the detonations are not completed, the rounds are

said to have detonated “low-order.” A percentage of fired rounds detonate low-order and the number varies substantially from one munition type to another (Dauphin and Doyle 2000). Over the past two decades, studies at over 30 military ranges have demonstrated the presence of energetic compounds in surface soils (Clausen et al. 2004; Pennington et al. 2005; Taylor et al. 2004; Ampleman et al. 2003a b; Jenkins et al. 2001, 1998; Thiboutot et al. 2003, 2000a,b, 1998). Further, these studies have confirmed that under ideal conditions a large percentage of the energetic material is consumed during detonation. However, these studies have also demonstrated that field conditions are not always ideal and consequently not all munitions undergo a high-order detonation thereby consuming all of the explosive material. A low-order detonation results in the distribution of energetic material into the environment as particulate (or bigger; Walsh et al. 2010) residues (Taylor et al. 2004; Hewitt et al. 2003; Jenkins et al. 2002) in an extremely heterogeneous manner (Jenkins et al. 1999; 1997a,b, 1996). Research over the last decade has demonstrated that special field sampling and sample preparation procedures are necessary to obtain a representative and reproducible results (Hewitt et al. 2009, 2007, 2005; Walsh et al. 2006a,b, 2005, 2003, 2002; Jenkins et al. 2006, 2005, 2004a,b, 2001, 1999; Hewitt and Walsh 2003; Thiboutot et al. 2002).

2.2 Sampling strategies for soils containing metallic residues

Conventional soil sampling procedures for environmental investigations often entail collecting grabs using either systematic–random sampling or biased–judgmental sampling. The former may be described as a “grid-node” approach; the area of interest is divided into a number of individual grids (exposure areas), the size of each being a function of the total area to be assessed and the future land use envisioned. Within each grid, one discrete sample is collected and shipped to an off-site laboratory where samples are processed and analyzed. Under the judgment sampling approach, an arbitrary number of discrete samples are collected from the area of interest. Often the sampling locations are determined by regulatory officials based on visual observations.

The results for these samples are assumed represent concentrations within the area of interest, and the concentrations of the individual samples are often assumed to be normally distributed. The results are subsequently used to calculate the mean concentration of the study area. Geostatistical approaches such as kriging may also be used to characterize the spatial

distribution of contamination (e.g., the concentration gradient between grid sampling points is assumed to be linear). However, the assumption that these discrete samples are “representative” of analyte concentrations within the area of interest is generally not tested, even though the concentrations of the discrete samples collected from within the same grid often do not agree. If enough discrete samples are collected, anomalous results are often evident during the geospatial analysis of the data. Then various ad-hoc approaches are used to adjust the data, e.g., calculating the mean of co-located samples results, assigning a value of $\frac{1}{2}$ the reporting limit to non-detect samples, etc.

Earlier research indicated that explosive concentrations in discrete samples can vary substantially even over short distances (Jenkins et al. 1999, 1997a,b) and energetic residues can be deposited at training ranges as discrete particles (Taylor *et al.* 2004). Studies within grids as small as 10×10 m using 100 discrete samples collected within a single 1×1 -m cell varied by two orders of magnitude and yielded percent Relative Standard Deviations (RSD) in excess of 100%; this demonstrates the short-range heterogeneity (Table 3). The reproducibility of a sample measurement is obtained by calculating the percent RSD of the samples,

$$\%RSD = 100 \times (s / \bar{x}) \quad (2)$$

where:

s = standard deviation (from variability of replicate multi-increment results)

\bar{x} = sample mean (mean of replicate multi-increment results)

A RSD of less than 30% for three to five replicates collected within the same Decision Unit (DU) is often considered to be indicative of an acceptable level of variability. However, note that this is only a “rule of thumb,” as decision errors actually depend on distribution of concentration measurements, as well as the magnitude of the differences between the concentration measurements and the levels of interest. As used in this document, the term DU (alternately termed “area of concern,” “sampling area,” “exposure unit,” “contamination zone,” “population,” or “habitat”) refers to the area that a sample is intended to represent.

Hewitt et al. (2009) suggest that if the %RSD is less than or equal to 30% for a set of replicate MI samples collected within the same DU, one could

assume a normal distribution and thus calculate a reliable upper confidence limit (UCL) for the DU mean. Although a <30% RSD cannot conclusively demonstrate that a distribution is normal, a larger %RSD would suggest deviations from normality and indicate that the field sampling design or laboratory processing, or both, were not adequate to control for the effects of heterogeneity in distribution or composition. Clearly, this is the case with the discrete samples shown in Table 3. The distributions for the discrete samples are non-Gaussian and positively skewed. Because the median concentrations are less than the mean, often much less, estimates of mean concentration from one or a few discrete samples nearly always underestimated the mean. Therefore, there is a concern about using discrete samples to represent the average concentrations in soil at firing points and impact areas. The extreme heterogeneity is ascribable to the presence of particles of energetic residues.

Table 3. Variability of soil concentrations among 100 discrete samples collected within 10- x 10-m grids at various training range impact areas from ERDC/CRREL TR-11-5 (Taylor et al. 2011).

Installation	Area*	Concentration (mg/kg)							RSD
		Range type	Analyte	Max	Min	Median	Mean	Std dev.	
Donnelly Training Area (AK) ¹	FP	Artillery	2,4-DNT	6.38	0.0007	0.65	1.06	1.17	110
CFB-Valcartier (QC) ²	FP	Antitank rocket	NG	2.94	0.02	0.281	0.451	0.494	110
CFB-Valcartier (QC) ²	IA	Antitank rocket	HMX	1150	5.8	197	292	290	99
Holloman AFB (NM) ³	IA	Bombing	TNT	778	0.15	6.36	31.8	87.0	274
Ft. Polk (LA) ⁴	IA	Mortar	RDX	2390	0.037	1.7	71.5	315	441
Cold Lake (AB) ⁵	IA	Bombing	TNT	289	0.38	6.57	16.2	32.3	199
Ft. Richardson (AK) ⁶	IA	Artillery	RDX	172	<0.04	<0.04	5.46	24.8	454
Ft. Richardson (AK) ⁷	IA	Mortar	RDX	4450	<0.04	<0.04	—**	—**	—**

*Firing point (FP) or Impact Area (IA). ¹ M.E. Walsh et al. 2004, ² Jenkins et al. 2004b, ³ Jenkins et al. 2006b, ⁴ Jenkins et al. 2004a, ⁵ Ampleman et al. 2003, ⁶ M.E. Walsh et al. 2007, ⁷ Hewitt et al. 2009 (Note: results from 200 discrete samples).
 ** — Not computed

To obtain representative and reproducible results, the sampling strategy must address the heterogeneity in composition and distribution of the constituents of concern (Pitard 1993). Compositional heterogeneity is attributable to soil-sized particles within the population not all having the same concentration. This heterogeneity is at a maximum when a portion of the contaminant is present as discrete particles.

Variability from compositional heterogeneity is called the Fundamental Error (FE) and is inversely related to the sample mass. Distributional heterogeneity is attributable to contaminant particles being scattered across the site unevenly, sometimes with a systematic component as well as a

short-range random component. Variability associated with distributional heterogeneity is inversely related to the number of individual increments used to build the sample. This type of variability is largest when a single discrete sample is used to estimate the mean of a large DU. To reduce the influence of distributional heterogeneity in the estimate of the mean concentration for a DU, the collection of 30 or more evenly spaced increments to form an individual soil sample has been recommended (Jenkins et al. 2006, 2005, 2004a,b; Hewitt et al. 2005; Walsh et al. 2005).

The objective of the MI approach (e.g., which typically uses systematic-random sampling) is to obtain a proportional amount of residue particles of every composition and shape. Instead of collecting and analyzing individual discrete samples and integrating the results over an area of interest (DU), or assuming that a single point represents the entire area, samples are prepared by combining a number of increments of soil from within the DU to obtain an approximately 1-kg sample. The increments can be collected using simple random sampling or systematic random sampling. For systematic random sampling, a random starting point is selected and evenly spaced increments are collected as the sampler walks back and forth from one corner of the decision unit to the opposite corner (Fig. 2).

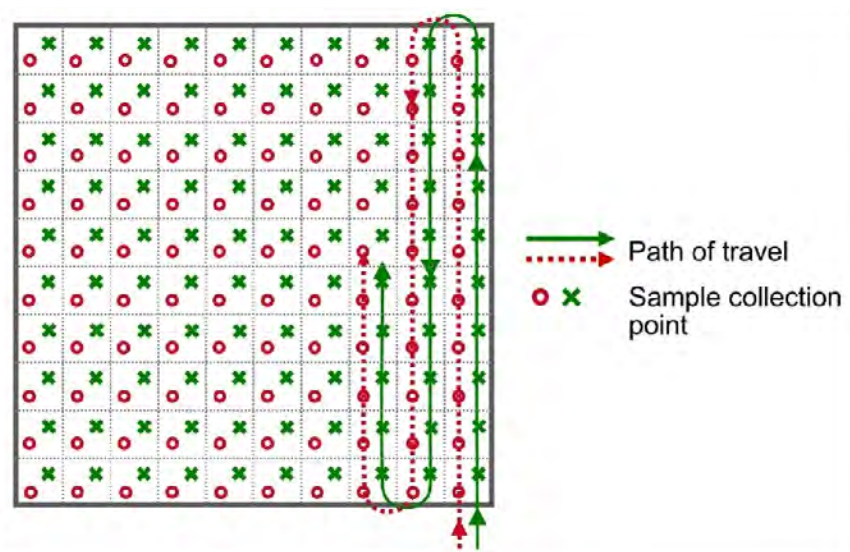


Figure 2. Example of multi-increment sampling using a systematic-random sampling design for collecting two separate 100-increment samples.

Subsequent studies using the MI sampling approach revealed reduced sample replicate variability as compared the grid-node sampling approach

(Nieman 2007; Jenkins et al. 2006, 2004a; Hewitt et al. 2005; Walsh et al. 2005). In addition, MI samples provided much more reproducible estimates of mean concentrations within DUs at firing point and impact areas than one or a few discrete samples (Table 4). Experiments were conducted at a variety of active training ranges to investigate the use of MI samples to obtain estimates of mean concentrations in areas varying in size from 10 × 10 m (100 m²) to 100 × 100 m (10,000 m²) (Table 4). The MI samples were often taken from the same DUs and at the same time as the discrete sample results listed in Table 3. In all cases the variability among replicate MI samples was much lower than for discrete samples taken within the same sample grids. Although the RSD for the Fort Polk MI sample is larger than what is typically preferred, it is nevertheless smaller the RSD for the discrete samples. Note, this particular MI sample consisted of 25 increments, suggesting that more increments were necessary to achieve a representative sample with an acceptable degree of variability.

Table 4. Variability of soil concentrations among multi-increment samples collected from grids at different ranges from ERDC/CRREL TR-11-5 (Taylor et al. 2011).

Installation	Area	Range type	Increments/ Sample	Number of Samples	Grid Size (m)	Analyte	Concentration (mg/kg)					(% RSD)
							Max	Min	Median	Mean	Std Dev	
Donnelly Training Area (AK) ¹	FP	Artillery	30	10	10 × 10	2,4-DNT	1.35	0.60	0.92	0.94	0.24	26
Holloman AFB (NM) ²	IA	Bombing	100	3	10 × 10	TNT	17.2	12.5	13.5	14.4	2.45	17
Ft. Polk (LA) ³	IA	Mortar	25	10	10 × 10	RDX	290	4.6	25	54	86	159
29 Palms (CA) ⁴	IA	Artillery/ Bombing	100	6	100 × 100	RDX	9.4	3.9	4.8	5.6	2.1	38
Hill AFB (UT) ⁵	TTA	Thermal treatment	100	3	100 × 100	HMX	4.26	3.96	4.16	4.13	0.15	4

* Firing point (FP), Impact Area (IA), or Thermal Treatment Area (TTA). ¹ M.E. Walsh et al. 2004, ² Jenkins et al. 2006b, ³ Jenkins et al. 2004a, ⁴ Hewitt et al. 2005a, ⁵ Nieman personal communication

The studies comparing discrete and MI sampling strategies for characterizing military training activities discussed earlier have shown that the distributions of data obtained from discrete samples tend to be non-Gaussian and positively skewed, whereas MI data are often normally distributed (Jenkins et al. 2006, 2005, 2004a,b; Walsh et al. 2005), a result that is consistent with the Central Limit Theorem of statistics. Moreover, a single discrete sample or small set of discrete samples often results in a lower estimate of the mean concentration than MI samples. The differences between the means determined from the discrete and MI sampling schemes become less pronounced as the number of discrete samples approaches the total number of increments collected for the set of MI samples. How-

ever, in general, the MI sample concentrations will be consistently less variable than the discrete sample concentrations.

The MI sampling method has been adopted as the accepted USEPA method (Method 8330B) for documenting deposition of particulate energetic residues on DoD training and testing range soils (USEPA 2006). Regulatory agencies and installation managers are attempting to apply the MI sampling methodology to other analytes, including metals (ITRC 2011; Alaska 2009, Hawaii 2008). Collecting a large number of unbiased increments (e.g., 30–100) over the entire DU (e.g., using simple or systematic–random sampling) is central to the MI sampling approach. To estimate the total uncertainty of the mean concentration of a munitions constituent, replicate MI samples must be collected with the DU. The U.S Geological Survey (USGS) recommends that the entire field sample be dried, passed through a no. 10 (2-mm) sieve, and then mechanically pulverized to reduce the particle size to < 0.15 mm (USGS 1993). This step is necessary because, within the < 2 -mm soil size class, particles of munitions constituents exist as a variety of sizes, densities, shapes, and compositions. The use of the no. 10 sieve targets those particles that more readily dissolve and is consistent with the classification of soil used in risk models for human exposure. Mechanical grinding of the sample to increase the number of particulate contaminants of interest in the sample is another essential part of the MI approach (ITRC 2011) to achieve a more homogenous analytical sample. It is also an important component of the energetics USEPA Method 8330B (USEPA 2006).

2.3 Metal residue deposition

Since the release of USEPA Method 8330B (USEPA 2006), a growing concern within the DoD, federal, and state agencies, has been that similar protocols should be adopted characterizing metals on training ranges and at other locations. The military routinely fires projectiles in training that contain metal in the casing body, slug, or as metal salts in fuzes and pyrotechnic formulations. Like energetics, metals at military ranges are expected to be spatially very heterogeneous. A wide variety of metals are used for military munitions. For example, the casing materials for most artillery and mortar projectiles consist of iron and manganese; the predominant metal in the anti-tank rockets is aluminum. The metals of interest at small arms ranges are primarily antimony, copper, lead, zinc (Clausen and Korte 2009a) and, in some situations, tungsten (Clausen and Korte 2009b;

Clausen et al. 2010, 2007). Pyrotechnic devices contain metal constituents such as aluminum, antimony, barium, boron, cerium, chromium, copper, iron, lead, magnesium, manganese, potassium, sodium, strontium, titanium, tungsten, zirconium, and zinc (Clausen et al. in review).

Anthropogenic metals are heterogeneously distributed over active training ranges as particles of various sizes, shapes, and compositions. The impact of heterogeneity on measured metal concentrations was assessed by comparing compares results obtained using different sampling methods from the same berm at a small arms range at Massachusetts Military Reservation (Table 5). The means for the MI samples are generally larger than the means of the discrete samples.

Table 5. Mean metal concentrations for different sampling methods at the Bravo Small Arms Range at Camp Edwards, Massachusetts.

Type	Discrete			Multi-increment		
Sample Design	Systematic Random	Biased	Large-mass	Biased	Systematic-Random	Systematic-Random
Increments per sample	1	1	1	15	100	50
Element	Concentration (mg/kg)					
Cr	<15	184	74	75	78	76
Cu	462	1555	569	984	643	709
Fe	6116	10,646	6686	7423	7392	7233
Mn	51	79	43	51	46	46
Pb	445	1182	952	945	339	357
Sb	16.3	31.4	25.4	23.3	15.8	15.2
W	666	1,479	581	1,247	787	783
Zn	38	135	32	41	32	43
Sample no.	8	8	1	1	2	2

Shaded text represents known contaminants of interest.

As munitions containing metals are frequently used on Army training lands (Fig. 3), it is expected the metals deposited by these rounds may build up in the soils and may need to be sampled (Fig. 4). The deposition of metals from this type of training has only been studied on a limited basis. The sampling design must address compositional and distributional heterogeneity to obtain representative samples (e.g., reproducible estimates of the mean). The sampling design must allow for acquiring an adequate number of particles of the constituents of interest in each sample and must ensure that the proportions of the various particles of interest in the samples are similar to the proportions of these particles in the envi-

ronmental population (DU). Thus, the average contaminant concentrations in the samples will be similar to the average concentrations in the population sampled. In the case of materials distributed non-uniformly, this objective results in samples of considerable mass (i.e., greater than 1 kg), each composed of 30 or more increments from evenly spaced locations throughout the DU. Traditionally, the analysis of metals in the environment has relied on much smaller sample masses, from which only a small portion is removed for further processing; less than 2 g of the parent sample is typically subsampled and subsequently digested and analyzed (USEPA 1996a,b). This research will assess the uncertainty associated with this traditional approach and demonstrate an innovative sampling strategy and sample-processing protocol that results in more reproducible metal concentrations for study areas.



Figure 3. Small arms projectiles found on a range at Fort Lewis, Washington.

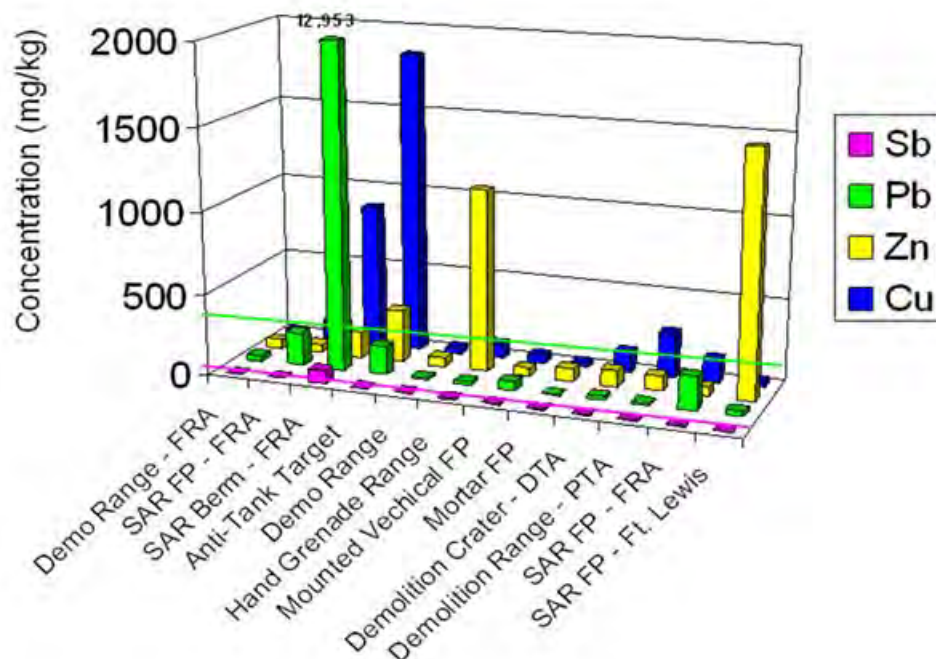


Figure 4. Surface soil metal concentration for different types of training ranges at a number of different military installations. Green line depicts the USEPA lead soil action level of 400 mg/kg.

Table 6. Replication of metal results (mg/kg) for co-located individual discrete soil samples from Bravo Small Arms Range at Camp Edwards, Massachusetts.

Element	Sample Identification							Mean (mg/kg)	Std. Dev. (mg/kg)	RSD (%)
	B8-A	B9	B10	B11	B12	B13	B14			
	Concentration (mg/kg)									
Al	4323	4202	5390	4983	4339	3605	5938	4676	801	17
Cu	84	257	430	2316	29	109	462	462	830	180
Fe	5691	5630	6811	6646	5628	4866	7774	611	999	16
Mg	602	793	962	974	733	723	1065	839	162	19
Mn	41	38	54	54	39	42	90	51	19	37
Pb	277	345	549	549	264	720	370	445	175	39
W	429	625	1374	1374	292	142	777	666	439	66
Zn	24.8	41.7	61.0	61.0	<15	16.5	35.4	37.7	15.9	42

Std. Dev. – standard deviation, Highlighted text indicates known contaminants of interest

Data from a limited study at the Bravo Small Arms Range at Camp Edwards, MA, using discrete samples and following the current sample processing methods yielded poor reproducibility of sample results, calling into question the representativeness of the data (Table 6). The samples were all collected within a 1- × 1-m square to a depth of 5 cm. At the present time,

the applicability of the special sample processing steps developed for energetics to soil samples containing metals is an unknown.

2.4 Study approach

Environmental studies of military training ranges have shown that energetic residues are heterogeneously distributed (Jenkins et al. 1999, 1997a, b, 1996). To representatively sample military ranges during site or remedial investigation activities MI sampling strategies have been recommended for the characterization of energetic residues (Hewitt et al. 2009). Members of the environmental regulatory community have accepted incremental sampling and the associated sample processing procedures for energetics (ITRC 2011; Alaska 2009; Hawaii 2008). These changes are documented in USEPA Method 8330B (USEPA 2006).

Because of the success of the MI methodology for energetics, members of the environmental community are considering its adoption for other hazardous residue constituents such as metals (Hewitt et al. 2011; ITRC 2011; Alaska 2009; Hawaii 2008). The current USEPA method for metals in soils is Method 3050B (USEPA 1996a). This project addresses whether changes to USEPA Method 3050B are necessary and whether improved data quality can be achieved by coupling MI sampling with adequate sample processing for determining mass loading of metal constituents on military training ranges. The working hypothesis is that the current field sampling and sample processing procedures for metals in soil do not yield representative and reproducible results for military sites where metal contamination is heterogeneously introduced into the environment as solid residues.

With this hypothesis in mind, the project evaluated potential modifications to field sampling and sample processing procedures to obtain representative samples of soils containing metal residues. MI sampling and adequate sample processing was demonstrated for characterizing soils containing metal residues released because of military training activities. Comparisons were made with existing protocols to evaluate data quality improvements. The field issues studied included the need for MI samples versus the traditional grab/discrete sampling approach. The optimum number of increments per sample was evaluated as well. Sample processing issues studied included:

1. Necessity of machining or grinding of the soil sample to reduce the size and increase the number of contaminant particles in the sample to reduce composition heterogeneity.
2. Appropriateness of field splitting.
3. Appropriate type of grinding apparatus.
4. Appropriate grinding interval.
5. Assessment of the need to increase the digested mass and digestion interval.
6. Optimum soil to acid ratio, i.e., digestion efficiency.

The optimum field sampling and sample processing procedures will be identified and submitted to the USEPA as a proposed method modification to USEPA Method 3050B. This research will assess the uncertainty associated with this traditional approach and demonstrate an innovative sampling strategy and sample-processing protocol that results in reproducible metal concentrations.

3 Methods

Anthropogenic metals are heterogeneously distributed over active training ranges as particles of various sizes, shapes, and compositions. To address the compositional and distributional heterogeneity associated with this form of dispersion, i.e., to establish a representative (repeatable) mean concentration, the sampling strategy and design must allow for acquiring an adequate number of particles of the constituents of interest so as to maintain their proportion relative to that existing in the decision unit. More simply stated, the average concentration in the sample should mimic the average concentration in the population sampled. In the case of materials distributed non-uniformly, this objective leads to a sample of considerable mass (i.e., > 1 kg) composed of 30 or more increments from evenly spaced locations throughout the decision unit. Traditionally, the analysis of metals in the environment has relied on much smaller samples. Typically, soil is collected in a 4-oz jar and subsequently sent to an environmental testing laboratory for analysis. At the laboratory only a small fraction of the soil sample is actually processed for analysis. The laboratory usually scoops no more than 1–2 g of soil from the top of the jar for extraction (acid digestion) by Method 3050B or Method 3051 (USEPA 1996a,b).

3.1 Field Sampling

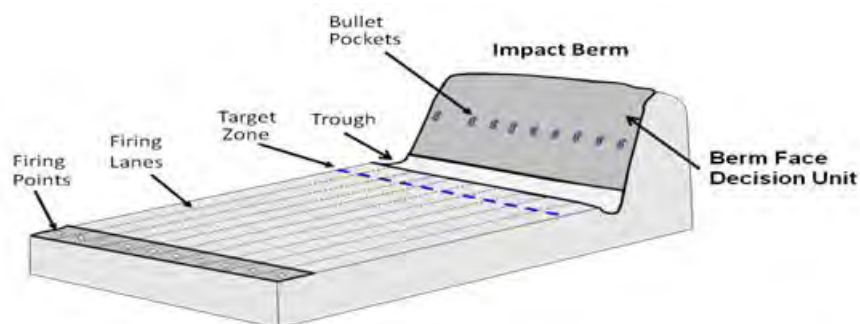


Figure 5. Schematic of decision unit sampled at Small Arms Range 4-3 at Camp Ethan Allen, VT.

Soil samples were collected from the berm face of Small Arms Range 4-3 at Camp Ethan Allen, VT (Fig. 5). This material was used to evaluate the appropriateness of applying USEPA Method 8330B sample collection, and processing procedures to soils containing metal residues and to evaluate possible modifications necessary to Method 3050B to achieve reproducible

and representative results. The soil material from this range can be classified as loamy sand (Fig. 6).

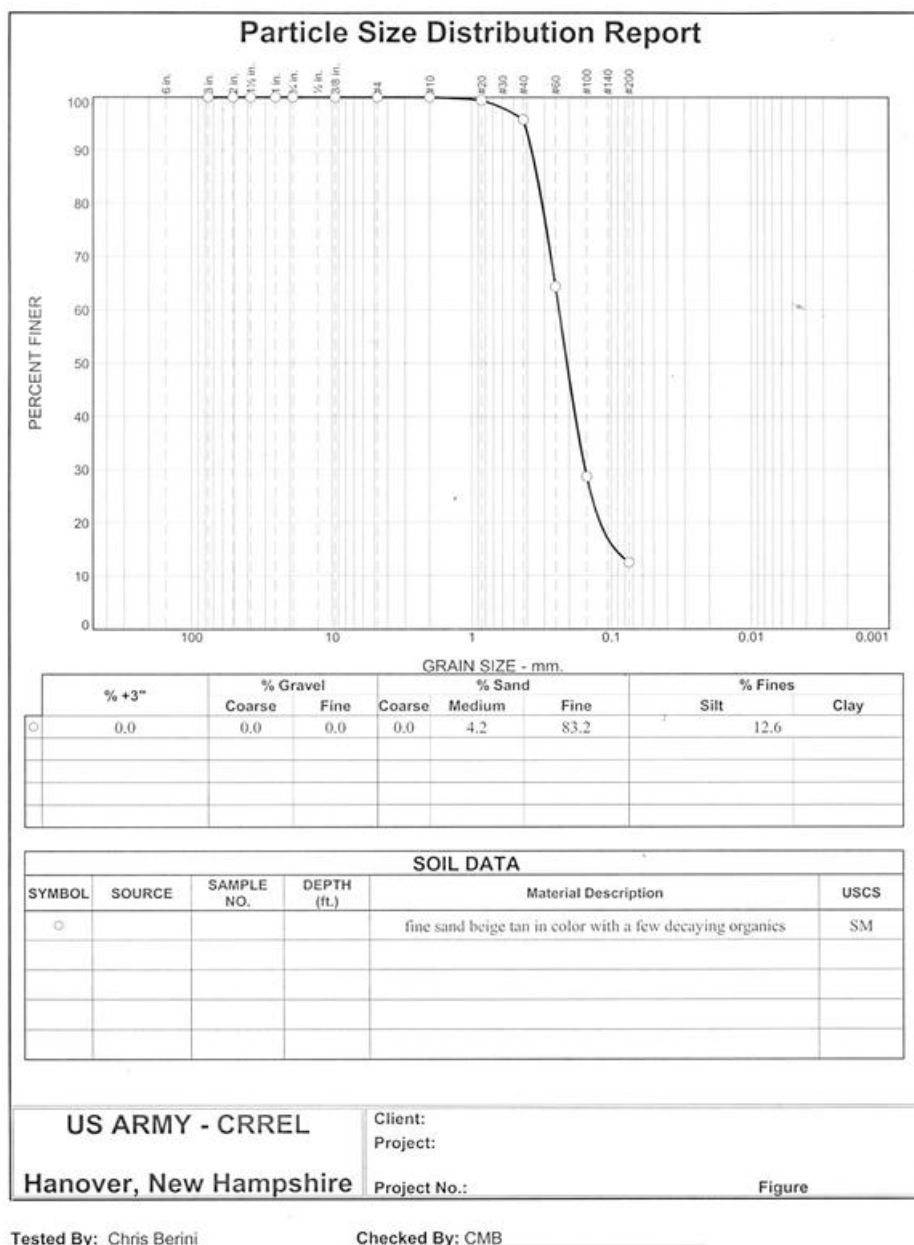


Figure 6. Particle size analysis for soil from Small Arms Range 4-3 at Camp Ethan Allen, VT.

Both MI and discrete surface soil samples were collected from Small Arms Range 4-3 on 30 June 2010. At the time of sample collection, the environmental conditions were sunny with a light wind and temperatures about 60°F (15.6°C). All samples were collected using the CRREL Multi-

Increment Sampling Tool (CMIST) (Fig. 7; Walsh et al. 2009) with the $\frac{3}{4}$ -in. (1.9-cm) corer diameter to a depth of 1 in. (2.5 cm) unless otherwise noted. The CMIST was used to extract cylindrical soil cores referred to as “increments.” Each individual increment typically weighed approximately 0.005 kg.

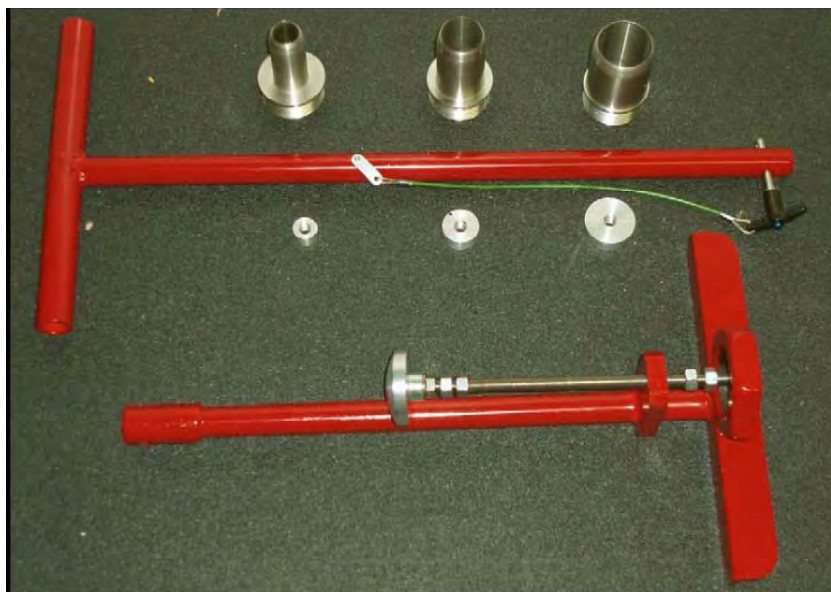


Figure 7. The CRREL Multi-Increment Sampling Tool. Coring tips are 2-, 3-, and 4-cm diameter (left to right). Corresponding disks are shown below the handle.

For discrete sample collection the berm face was gridded into 30 individual sample areas (Fig. 8) with a single increment collected from the center of each grid and placed into individual 4-oz amber glass jars. Forty-three MI samples were collected over the entire berm face (the DU).

30	27	24	21	18	15	12	9	6	3
29	26	23	20	17	14	11	8	5	2
28	25	22	19	16	13	10	7	4	1

Figure 8. Location of discrete samples collected on the berm face at Small Arms Range 4-3 at Camp Ethan Allen, Vermont.

The first sample consisted of our test material to evaluate the different sample preparation methods. Because a large volume of soil was needed, 200 increments were collected from the DU using a 1.5-in. (3.8-cm) diameter CMIST to a depth of 3 in. (7.6 cm). To evaluate the number of increments per DU, sets of replicate MI samples were prepared from 5, 10, 20, 30, 50, and 100 increments. Seven replicates were collected for each increment grouping.

3.2 Laboratory sample preparation

All soil samples were transported to CRREL in Hanover, NH. The purpose of the project was to compare the conventional discrete sampling approach with the MI sampling approach and evaluate changes to laboratory sample processing procedures that may be needed to improve the quality of the results. Figure 9 is a conceptual representation of the overall experimental design. Soil samples were transported to CRREL and air-dried on aluminum trays. Once air-dried, each sample was passed through a no. 10 (2-mm) sieve. The weights of the < 2 mm and > 2 mm size fractions were recorded. The < 2 mm size fraction was typically ground using a Lab Tech Essa chrome steel ring mill grinder (Model LM2, Belmont, Australia), except for those cases requiring an unground sample or the evaluation of different milling equipment. The chrome steel bowl and puck were cleaned after each grind by washing with soapy water, followed by an acetone rinse and air-drying. The digestion of the soil samples generally followed USEPA Method 3050B with various modifications tested and discussed in the following subsections.

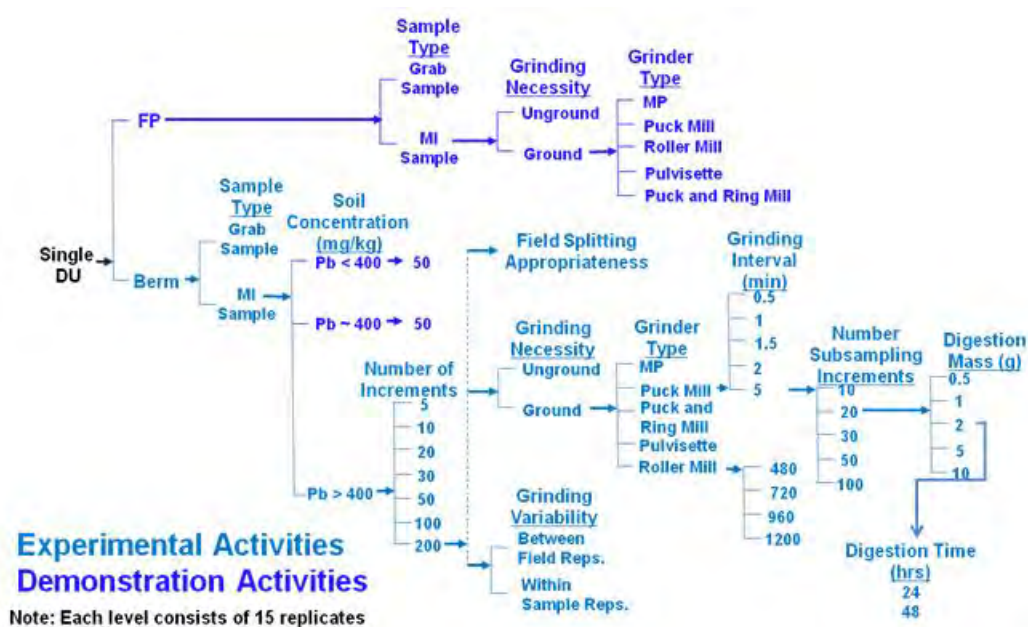


Figure 9. Proposed experimental design.

3.2.1 Experiment 1—glass as a quality control medium

The suitability of glass beads as a quality control medium was evaluated (e.g., for the preparation of method blanks). Glass beads of 5-mm diameter

(Kimble Kontes, No. 13500-5) were used. The metal content of the glass beads was first determined using the soil digestion procedure USEPA Method 3050B. The glass beads were subsequently washed with aqua regia, a solution of 100 mL of hydrochloric acid and 300 mL of nitric acid (trace grade for each). The acid solution was added to a jar containing the glass beads and swirled for approximately 1 minute. The acid was then decanted and the glass beads rinsed with de-ionized (DI) water three times, decanting the DI water after each rinse. The washed glass beads were then ground in the puck mill and digested using USEPA Method 3050B. Glass beads were also ground in the puck or ball mill as a control and then washed, digested, and analyzed. This was followed by grinding of a soil sample and then grinding several batches of glass beads in sequential order to assess the possible cross-contamination from the grinding apparatus.

3.2.2 Experiment 2—Multi-increment vs. traditional discrete/grab sampling

This experiment evaluated the representativeness and reproducibility of soil sample results using the MI approach versus the traditional discrete/grab sampling approach. Three replicate systematic-random MI samples, consisting of 100 increments, were collected (Fig. 2 and 5). With a grid-node approach, 30 grab samples were also collected (Fig. 8) from the same DU from which the MI samples were collected and placed in an amber 4-oz container.

The objective of this experiment was to evaluate whether MI sampling results in better precision than discrete samples. This involved evaluating sample-to-sample variability using three multi-increment field replicates, and evaluating within sample variability using 15 laboratory replicates prepared from a single MI sample. The discrete samples were used to assess the variability between samples across the DU.

The standard procedure followed for sample preparation of the MI samples in this experiment and most of the subsequent experiments followed the description in Section 3.0. A sub sample of the < 2 mm ground material was prepared using 20 increments to build a 2-g digestion mass. The volume of each digestate (an aqueous solution of HNO₃ and HCl) was adjusted to 50 mL per USEPA Method 3050B (USEPA 1996a). The digestate

was analyzed using an inductively coupled plasma-optical emission spectrometer (ICP-OES) using USEPA Method 200.7 (USEPA 1994).

The discrete/grab samples were sent to CRREL and air dried and sieved with a no. 10 (2-mm sieve). The > 2-mm portion was set aside. The < 2 mm portion was ground using a mortar and pestle for 1 minute and then placed back in the 4-oz jar. Two grams of material were scooped off the top of the sample container for digestion, the typical sub-sampling procedure for commercial analytical laboratories. One of the 30 discrete samples was subsampled to prepare a set of 15 replicates by taking 15 individual scoops out of the same jar. Digestion and analysis followed the same procedures as used for the MI samples, with the exception that a single 2-g sample was obtained from the 4-oz jar.

3.2.3 Experiment 3—number of increments per decision unit

One of the questions about the MI sampling methodology is how many increments need to be collected for each MI sample. This issue has not been satisfactorily studied, even as part of CRREL's previous work with energetics (Jenkins et al. 2005; Walsh et al 2005). The general rule of thumb adopted by CRREL is that 100-increments should be collected. USEPA Method 8330B (USEPA 2006) and Hewitt et al. (2009) recommend a minimum of 30-increments be collected. However, the question of number of increments to collect is routinely raised in meetings with military installations, regulators, and consultants with a desire to decrease the number of increments collected.

The objective of this experiment was to determine the minimum appropriate number of increments per DU to obtain a representative sample (e.g., to determine if at least 30 increments are needed to obtain reproducible results) The performance criteria consisted of 30% RSD for samples having the same number of increments and a statistically significant decrease in variance at the 95% confidence level between the smallest number of increments and each subsequent increase in the number of increments.

The same sampling approach used in Experiment 1 was used to acquire samples for Experiment 2. However, seven replicate MI samples prepared from 5, 10, 20, 30, 50, and 100 increments were collected from within the DU. This resulted in six sets of seven MI replicates—one for each “increment class/grouping.” In this case, sample mass was not controlled (as the

mass of each MI sample is proportional to the number of increments collected). Once collected, the MI samples were processed following the methodology in Section 3.0. Each subsample was obtained by randomly collecting 20 increments from the ground soil to build a 2-g mass. The subsamples were digested using 3050B. The final digestate volumes were 50 mL. The digestates were analyzed using an ICP-OES. One MI replicate for each increment class was subsampled to create 15 replicates.

3.2.4 Experiment 4—field splitting

One of the current issues with MI sampling is the large volume of soil collected and submitted to the analytical laboratory. Many analytical laboratories are not equipped to handle large volumes of soil. Some environmental companies recommend that samples be split in the field using cone-and-quartering techniques or a riffle splitter to reduce the sample volume. However, the appropriateness of applying field splitting techniques is questionable (USEPA 2003) based on past work with energetic materials (Hewitt et al. 2009) and preliminary studies with metals (Table 7).

Table 7. Laboratory splitting error for an unground soil sample from a small arms range using a rotary splitter.

Replicate	Split 1		Split 2	
	Cu (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Cu (mg/kg)
1	2600	360	5.5	99
2	110	330	5	90
3	300	920	7.6	87
4	110	300	4.3	99
5	130	280	4.3	130
6	140	2,800	16	90
7	860	1600	12	88
8	540	330	4.6	99
9	1200	850	4.2	83
10	130	1500	4.5	98
11	1900	380	4.9	99
12	120	330	4.3	110
13	130	290	3.7	80
14	120	300	4.1	87
15	110	820	8.2	84

Table 7 presents results from a MI soil sample that was collected from a military small arms range. The sample (over 1 kg of soil) was air-dried and sieved. The < 2-mm unground portion was then divided into multiple splits using a sectorial splitter, a device known to outperform cone and quartering by a wide margin. Each split was then sampled using 20 increments to build 2-g subsamples. The subsamples were digested following USEPA Method 3050B (USEPA 1996a) and analyzed using an ICP-OES following USEPA Method 6010. Order of magnitude differences are evident in the data, suggesting that the results are neither reproducible nor representative of the metal content in the site soil. The USEPA action level for lead is 400 mg/kg. Depending on which split was selected different actions would be necessary—no action versus soil clean up.

A study was conducted to assess the impact of using cone-and-quartering to obtain representative and reproducible results prior to machining the sample, as this is a commonly used method in the environmental industry even though Gerlach and Nocerino (2003) and Pitard (1993) indicate that this method yields unacceptable results. The test soil for this experiment and all subsequent experiments (4–10) involves the collection of a 200-increment soil sample yielding 25 kg of material from the small arms range berm at Camp Ethan Allen, VT. The test soil was collected and then split in the field using a cone-and-quartering technique. After splitting, each quarter was dried and then sieved with a no. 10 (2-mm) sieve. The > 2-mm size material was set aside. The < 2-mm portion of each quarter was ground separately in a puck mill for five 60-second intervals. Fifteen 2-g replicates from each quarter were collected through subsampling using 20 increments. The digestates were brought up to a 50 mL volume using HNO₃ and HCl per USEPA Method 3050B (USEPA 1996). The digestates were analyzed using an ICP-OES.

The objective of this experiment was determining if field splitting prior to machining is possible to reduce sample volume sent to the laboratory for processing. The performance criterion consists of 15% RSD for each quarter and no statistically significant difference between the means of each quarter at the 95% confidence level.

3.2.5 Experiment 5—sample pulverization necessity

One of the issues identified with energetic particle distribution was the high degree of heterogeneity observed in collected soil samples. Prelimi-

nary data indicate the issue of sample heterogeneity applies to situations where metal residues are deposited in the environment. Consequently, there may be a need to reduce the particle size of the sample to achieve a representative result. A limited study of a berm where small arms and 40-mm rocket-propelled grenades were fired into at Fort Wainwright, AK, suggests milling is necessary to reduce the impact of heterogeneity within the sample (Table 8). The Al and As constituents are associated with the grenade casing and Pb, Cu, and Zn with the small arms munitions.

To assess milling necessity the 200-increment sample was utilized. The sample was dried, sieved with no. 10 (2 mm) sieve, and the < 2-mm portion was split into two equal parts using a sectorial splitter. The > 2-mm size portion was set aside. One set of the < 2-mm samples was not ground and the other set ground 5 × 60 s in a puck mill. Then, 15 replicates were built by sub sampling each using 20 increments to build a 2-g digestion mass which, after digestion, was brought up to a final volume of 50-mL using HNO₃ and HCl per USEPA Method 3050B. The digestate was analyzed using an ICP-OES.

Table 8. Unground and ground soil samples for a berm at Fort Wainwright, Alaska.

	Statistic	Analyte (mg/kg)				
		Al	As	Cu	Pb	Zn
Unground (n=7)	Mean	9730	8.7	337	4380	71
	Std. Dev.	411	2.9	236	6660	29
	RSD (%)	4	33	70	152	40
Ground (n=7)	Mean	12,000	8.1	420	1560	81
	Std. Dev.	422	0.66	228	172	25
	RSD (%)	4	8	54	11	31

RSD – percent relative standard deviation

Std. Dev. – standard deviation

The objective of this set of experiments was to determine if milling is necessary to yield a representative sample. The performance criteria consisted of 15% RSD for each population and no statistically significant difference between the mean of the unground and ground populations at the 95% confidence level. The bias for the mean concentration of the ground samples should be < 30% of the mean of the unground samples.

One of the issues associated with pulverizing soil samples to reduce particle size with a metallic grinder was the introduction of metals from the grinder to the sample. The cross contamination issue was also assessed as part of the experiment discussed above. Following drying, sieving, and grinding, three separate aliquots of glass beads were ground following the procedures in Test 2 in sequential order, i.e., clean the bowl and puck using the normal CRREL procedure following the soil grinding and then grind 3 separate sets of glass beads. The objective of this experiment was to determine if metal carryover occurs using the puck mill. This same test was also conducted with the puck and ring mill and ball mill at Test America and the pulvisette at ERDC's Environmental Laboratory (EL). The ball mill and pulvisette both consist of non-metallic materials so they will act as a control for comparison with the puck and puck and ring mill grinders.

3.2.6 Experiment 6—grinder type evaluation

If sample pulverization was needed to address sample heterogeneity, appropriate grinding equipment was necessary. By use of the same 200-increment reference soil from the small arms range at Camp Ethan Allen, the sample was dried and then sieved with no. 10 (2-mm) sieve. A rotary splitter was used to separate the < 2-mm soil portion into seven different splits. One split consists of the unground sample (control). The other five splits were ground with the following:

1. Mortar and pestle (at CRREL).
2. Pulvisette at EL in Vicksburg, MS) with agate ball and bowl.
3. Roller (ball) mill (at Test America) with ceramic balls and polyethylene lined steel cans.
4. Ring and puck mill (at Test America).with chrome steel bowl, ring, and puck
5. Puck mill (at APPL Labs) with chrome steel bowl and puck.
6. Puck mill (CRREL) with chrome steel bowl and puck.

Each experiment used a grind interval of 5×60 s, except for the roller mill, which used an interval of 18 hours. At the end of each grind interval of 60 s the material was passed through a no. 120 (0.125 mm) sieve. The mass of the fraction passing through the sieve and the mass of the remaining fraction on top of the sieve were recorded for each grinding device and split to support a qualitative assessment of the efficiency of the grinding process. Once the samples were ground, 15 replicates of each ground split

were collected by sub-sampling using 20 increments to build 2-g digestion masses. The samples were digested following the methodology in USEPA Method 3050B. The digestates were analyzed by ICP-OES.

The LM-2 puck mill used at CRREL to mill the < 2 mm soil fraction contains metallic components that are in contact with the soil being ground. The metal content of the bowl is summarized in the Table 9.

Table 9. Metal content of puck mill bowl.

Metal	Concentration (mg/kg)*
Cr	1×10^5
Cu	1990
Fe	5×10^5
Mn	3700
Ni	3030
Pb	7
Sb	18
V	1140
W	1210
Zn	52

* Values supplied by Land Tech Essa.

The same puck mill brand and model was used by APPL Inc. The ring-and-puck mill used by Test America is a TM Engineering ring-and-puck mill grinder (Model TM/S). The ball mill grinder used by Test America is a US Stoneware roller mill (Model 803FVM), consisting of steel cans with ceramic grinding stones.

The objective of this experiment was to determine which grinding apparatus yields acceptable results. The performance criteria consist of 15% RSD for samples ground with the same apparatus and no statistically significant difference of the means, at the 95% confidence level, between the CRREL puck mill and the unground samples and the puck mill and other grinders. Additionally, the mean positive concentration bias for the ground population should be less than 30% of the unground mean.

3.2.7 Experiment 7—grinding interval

Under the assumption that milling is necessary to overcome sample heterogeneity, the question remains how long samples should be ground. Previ-

ous work with explosive residues indicated a grinding time of 60 s is necessary to reduce the particle size such that the sample yields reproducible results (Hewitt et al. 2009; Walsh et al. 2002, 2005, 2006a). Studies with propellant residues indicated longer grind intervals of 300 s are necessary (Walsh et al. 2006a). Because, the grinding process generates heat and some energetic analytcs are susceptible to heat degradation, a cooling interval is used. The recommended grinding process involves a 5×60 s grind with a several minute cooling interval between grinds (Hewitt et al. 2009; USEPA 2006; Walsh et al. 2006a). Because firing point soils at small arms ranges contain both propellant and metal residues, a single grinding process is desired to address the heterogeneity issues for both residue constituents. The grinding interval optimization experiment was conducted with the puck mill at CRREL and the roller mill at Test America.

With the same 200-increment reference soil from the small arms range at Camp Ethan Allen being used, the sample was dried and then sieved with no. 10 (2-mm sieve). A rotary splitter was used to separate the < 2 -mm soil fraction into 10 different splits. One < 2 mm split consists of the unground soil. Five splits were ground using intervals of 30, 60, 90, 120, and 300 s in the puck mill. The same procedures were used to prepare the samples prior to grinding with the roller mill. The grinding intervals evaluated with the roller mill were 8, 12, 16, and 20 hr. Once the samples were ground, 15 replicates of each sample were built by subsampling, using 20 increments to build 2-g digestion mass. The samples were digested following USEPA Method 3050B and analyzed by ICP-OES.

The objective of this experiment was to determine the optimum-grinding time for the puck and roller mills to yield reproducible results. The primary performance criteria consist of 15% RSD for samples of the same grinding interval and statistically significant decreases in variance at the 95% confidence between the unground sample and the shortest grind interval or between the shortest grind interval and each subsequent increase in grinding interval. A secondary performance criterion is identifying the grinding time that does not result in statistically significant increases in metal concentrations at the 95% confidence level when comparing the individual grind intervals. The optimum grinding interval may not be the same for all grinder devices, as well as for all small arms range metals or other types of military activity where metal residues are introduced to the

environment. Therefore some compromises may be necessary on the preferred grinding interval.

3.2.8 Experiment 8—optimum digestion mass

USEPA Method 3050B (USEPA 1996a) recommends a digestion mass of 1 to 2 g and USEPA Method 3051A and 3052 recommends a 0.5-g digestion mass (USEPA 1996b,c). Previous studies with energetic materials determined that an increase in extraction mass from the standard 2 to 10 g was necessary to decrease the sampling error (Hewitt et al. 2009; Walsh et al. 2002). As a consequence, the modified USEPA Method 8330B for energetics now specifies an extraction mass of 10 g (USEPA 2006). The thought was that the same issues observed with energetics may apply to metals. Therefore, a study was done to evaluate this issue. All of the sample collection and preparation procedures up to the subsampling to build the digestate discussed in the previous experiments were followed. Seven replicates were created by subsampling using 20 increments to yield masses of 0.5, 1, 2, 5, and 10 g. The acid ratio specified in Method 3050B was adjusted proportionally for the sample masses that were digested. The samples were digested following USEPA Method 3050B and analyzed by ICP-OES.

The objective of this experiment was to determine if the sampling error is reduced by increasing the digestion mass if all other conditions such as digestion efficiency and digestion mass remain the same and whether the existing USEPA Method 3050B recommendation of 1 to 2 g (USEPA 1996a) or 0.5 g, USEPA Methods 3051A or 3052 (USEPA 1996b, c), digestion mass is sufficient. This test assessed the combined effects of digestion mass and digestion efficiency. The primary performance criteria consist of 15% RSD for samples of the same digestion mass and a statistically significant decrease in variance at the 95% confidence when the digestion mass is increased. The primary performance criteria will be identifying the digestion mass that does not result in a statistically significant increase in metal concentration at the 95% confidence level when comparing the individual digestion masses.

3.2.9 Experiment 9—sensitivity to different digestion intervals

The current digestion procedure in USEPA Method 3050B (USEPA 1996a) typically requires a day to complete. However, in a production laboratory setting, it is not uncommon to have samples sit overnight in the digestion

block or even through a weekend. One of the issues raised was whether there was a significant increase in metal concentration with increasing digestion time. All of the sample collection and sample preparation procedures utilized in previous experiments were followed for Experiment 9 up to the digestion step. One set of 15 replicates of the same sample was digested in a day (12 hours). The other set of 15 replicates of the same soil were digested over 24-hr.

The objective of this experiment was to determine if digestion time significantly affects digestion efficiency (e.g., the effect of increasing the digestion time for the reported concentrations). The intent is to perform an initial assessment to determine if a more comprehensive study (e.g., using multiple digestion intervals) is likely needed. The null hypothesis is that increasing the digestion time was not result in a statistically significant increase in the mean concentration at the 95% confidence level.

3.3 Analysis

The digested soil samples were analyzed for metals at either EL or CRREL. EL used a Perkin Elmer Sciex ELAN 6000 inductively coupled plasma mass spectrometry (ICP-MS) instrument following USEPA Method 6020. CRREL used a Thermo Fischer ICAP 6300 Duo view ICP spectrometer equipped with a CETAC ASX-520 auto sampler per USEPA Method 6010. The operating conditions were set as follows: RF power at torch, 1150W; auxiliary gas flow rate 0.5 L/min, nebulizer gas flow rate, 0.7 L/min and pump flow rate of 50 rpm.

ICP/MS analysis of samples performed at Test America used an Agilent 7500 Series inductively-coupled plasma mass spectrometer in the collision-cell mode, with helium as the collision gas following USEPA Method 6020.

Samples were analyzed at APPL Inc, according to EPA 6020, using an ICP-MS (Agilent 7500cx ICP-MS equipped with an Agilent ASX-500 series ICP-MS auto sampler). The operating conditions were set as follows: RF power at torch = 1600 W, carrier gas flow = 1 L/min., auxiliary gas flow = 0.1 L/min., nebulizer flow = 0.4 mL/min., and pump flow rate = 0.1 rpm.

4 Results

4.1 Glass bead

There is a necessity for assessing the metal carryover from grinding equipment containing metal components when pulverizing soil and analyzing for metal content. Previous work by Clausen et al. (2010) established that Ottawa sand material was unsuitable as a quality control medium owing to the high metal content of the sand, inconsistent metal levels between different sand lots, and high degree of metal heterogeneity within a particular sand lot.

One possible material explored was commercially produced glass beads or soda glass obtained from crushing laboratory grade clear-glassware. The latter was explored by Test America (data not reported) and appears to be a suitable material. However, there is a potential safety issue during the process of crushing the glass to introduce into the puck mill. It is less of an issue if the glass is pulverized within a ball mill, as the intact glassware can be placed directly in the ball mill jar. The tests below discuss the use of 5-mm glass beads. One potential drawback for the use of glass beads is the cost, which could be significant for commercial laboratories when large numbers of soil samples are processed, requiring a large number of quality control samples (e.g., method blanks prepared from crushed glass).

A statistical summary of concentration of metal in unground unwashed glass beads, unground washed glass beads, ground unwashed glass beads, and ground washed glass beads is presented in Table 10. All of the analytical data are provided in Appendix A. The concentration of the metals of interest (Sb, Cu, Pb, and Zn) for the unground glass beads and washed beads was < 1 mg/kg, except for Cu. The mean Cu concentration for the unground glass beads was 1.20 mg/kg and the concentration of the washed material was 1.18 mg/kg. The metals with concentrations > 1 mg/kg were Al, Fe, Mg, and P. Tungsten was not detectable in any of the unground samples at the reporting limit of 0.16 mg/kg. The washing procedure for the glass beads is discussed in Section 3.2.1. The washing procedure reduced the metal content of the unground glass beads.

Next, the glass beads were ground in CRREL's puck mill and then analyzed for the metal content (Table 10). In all cases, the metal concentration in-

creased as a result of grinding, with Al, Cr, and Fe levels increasing substantially as compared to the unground samples. Tungsten was not detected in any of the ground glass samples. Lab Tech Essa indicates that the following metals are present in the alloy used to make the ring and bowl: Al, Cr, Cu, Fe, Mn, Ni, Pb, Sb, V, W, and Zn. All four small arms range metals of interest are included in this list. Washing the ground glass reduced the metal content, with Ba, Cd, Co, Cu, Mg, Mn, Sb, Sr, and Zn levels comparable to the unground glass material. The Pb level of the washed glass was 0.470 mg/kg as compared to 1.93 mg/kg for the unwashed ground glass. The washed ground glass Pb level was slightly higher as compared to the unground glass (0.135 mg/kg) and the washed unground glass (0.063 mg/kg). Washing the ground glass substantially reduced the level of Al, Cr, and Fe, although the levels remain elevated above the unground glass material concentration.

The length of puck mill grinding interval and its impact on the metal concentration of washed ground glass beads were assessed (Table 11). The concentration of Al, Cr, Fe, Mg, Mn, K, and Na increased slightly with a longer grinding interval and Cu decreased slightly. The remainder of the metals were unchanged as result of milling.

Table 10. Summary of metal levels for unground glass beads, unground washed glass beads, ground glass beads, and washed ground glass beads.

Treatment	Sample statistic	Concentration (mg/kg)															
		Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	Zn
Unground Glass	<i>n</i>	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	Mean	2.84	0.153	ND	ND	0.020	1.20	2.87	7.21	0.075	0.033	2.25	0.135	0.045	0.078	ND	0.603
	Median	2.84	0.153	ND	ND	0.020	1.20	2.87	7.21	0.075	0.033	2.25	0.135	0.045	0.078	ND	0.603
	Min	2.45	0.140	ND	ND	0.010	1.16	2.55	6.48	0.075	0.020	1.96	0.085	0.030	0.075	ND	0.520
	Max	3.22	0.165	ND	ND	0.030	1.25	3.19	7.94	0.075	0.045	2.54	0.185	0.060	0.080	ND	0.685
	STD	0.544	0.018	ND	ND	0.014	0.064	0.453	1.03	0.000	0.018	0.414	0.071	0.021	0.004	ND	0.117
	RSD (%)	19	12	ND	ND	71	5	16	14	0	54	18	52	47	5	ND	19
Unground Glass Washed	<i>n</i>	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	Mean	2.01	0.095	ND	ND	ND	1.18	1.84	5.38	0.023	ND	2.55	0.063	ND	0.050	ND	0.407
	Median	1.93	0.100	ND	ND	ND	1.19	1.85	5.43	0.025	ND	2.49	0.065	ND	0.050	ND	0.445
	Min	1.87	0.085	ND	ND	ND	1.15	1.73	4.99	0.020	ND	2.40	0.055	ND	0.050	ND	0.225
	Max	2.22	0.100	ND	ND	ND	1.22	1.96	5.73	0.025	ND	2.77	0.070	ND	0.050	ND	0.550
	STD	0.189	0.009	ND	ND	ND	0.035	0.115	0.372	0.003	ND	0.193	0.008	ND	0.000	ND	0.166
	RSD (%)	9	9	ND	ND	ND	3	6	7	12	ND	8	12	ND	0	ND	41
Ground Glass	<i>n</i>	18	18	15	18	18	18	18	18	18	18	18	18	18	18	18	18
	Mean	128	0.660	0.042	0.129	60.9	1.86	456	8.42	3.64	0.700	2.36	1.93	0.827	0.187	0.045	0.985
	Median	126	0.658	0.040	0.119	56.9	1.90	424	8.32	3.45	0.618	2.06	1.92	0.710	0.185	0.045	0.911
	Min	104	0.595	0.035	0.100	51.1	1.71	380	7.53	3.10	0.495	1.84	1.19	0.580	0.165	0.035	0.610
	Max	150	0.780	0.057	0.200	90.6	1.98	692	9.39	5.11	1.14	4.30	2.96	1.83	0.219	0.065	1.560
	STD	12.5	0.038	0.006	0.032	13.7	0.09	108	0.48	0.68	0.205	0.788	0.49	0.316	0.012	0.007	0.242
	RSD (%)	10	6	15	25	23	5	24	6	19	29	33	26	38	6	16	25
Ground Glass Washed	<i>n</i>	18	18	15	18	18	18	18	18	18	18	18	18	18	18	18	18
	Mean	30.0	ND	0.03	ND	4.86	1.56	27	4.60	0.357	0.722	1.84	0.470	0.040	0.078	ND	0.408
	Median	30.3	ND	0.03	ND	3.90	1.55	23	4.55	0.255	0.170	1.67	0.468	0.020	0.078	ND	0.393
	Min	22.3	ND	0.02	ND	2.92	1.40	17	3.60	0.205	0.010	1.51	0.240	ND	0.065	ND	0.220
	Max	37.5	ND	0.05	ND	10.4	1.96	52	5.40	0.900	3.74	2.93	0.780	0.175	0.095	ND	0.605
	STD	4.26	ND	0.01	ND	2.52	0.136	11.7	0.441	0.247	1.33	0.465	0.139	0.061	0.007	ND	0.103
	RSD (%)	14	ND	30	ND	52	9	44	10	69	184	25	30	154	9	ND	25

n – sample size (replicates), Min – minimum, Max – maximum, RSD – relative standard deviation, STD – standard deviation,
 ND = Non-detects precluded calculation of summary statistics
 Highlighted text represents those metals present in the chrome steel puck and bowl for the Lab Tech Essa puck mill

Table 11. Impact of puck mill grinding interval (s) on measured mean metal value (mg/kg) of washed ground glass beads.

Grinding Interval	n	Mean Concentration (mg/kg)																			
		Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	K	Na	S	V	W	Zn
60	3	1.65	ND	0.581	ND	ND	1.39	0.116	10.7	0.118	ND	ND	ND	ND	3.23	14.7	ND	ND	ND	ND	
2 x 60	3	2.26	ND	0.527	ND	ND	2.43	0.111	18.5	0.121	0.150	ND	ND	ND	ND	4.30	20.8	ND	ND	ND	ND
3 x 60	12	2.74	ND	0.554	ND	ND	2.97	0.098	22.4	0.127	0.180	ND	ND	ND	ND	5.10	24.8	ND	ND	ND	ND

n – number, ND – Non-detected precluded calculation of mean,
Highlighted text indicates known metals present in the chrome steel bowl and puck for the Lab Tech Essa Puck Mill

4.2 Multiple increment vs. grab (discrete) samples

The standard sampling approach utilizing grab/discrete samples was compared with samples collected using the MI methodology. The different sampling approaches consisted of collection of 30 grab samples using a gridded systematic process, six biased grab samples, and seven 100-increment samples. The sampling and sample preparation methodology is discussed in Section 3.2.

Briefly, the grab surface soil samples were collected from the small arms range berm face at Range 4-3 DU located at Camp Ethan Allen, VT, with the CMIST and placed in 4-oz jars. Thirty individual grab soil samples were collected from 0 to 2 in. using a 1-in. CMIST corer following a grid-node sampling approach and six grab samples were collected using a biased sampling approach. Each of these samples consisted of approximately 200 g of material. The soil samples were air-dried, sieved to remove the > 2mm fraction; the < 2 mm was ground in a mortar and pestle for 1 minute. No further processing of the sample was done prior to digestion and they were placed back in the original 4-oz containers to scoop 2-g of soil off the top. The manner in which the grab samples were processed exceeds what commercial laboratories generally do; namely, they do not typically sieve and grind the samples prior to subsampling to obtain subsamples that are more representative. Commercial laboratories typically take the subsample directly from the 4-oz jars. The digestion procedures followed USEPA Method 3050B with no modification and then analysis was performed by ICP-OES using USEPA Method 6010.

The MI surface soil samples were collected from the same DU as the grab samples with 100 increments collected using the CMIST sampler following a systematic-random sampling approach. Each of the three field replicate samples consisted of approximately 1 kg of material. The multiple incre-

ment samples were air-dried and sieved. The < 2 mm size fraction was ground in the puck mill for 5×60 s and then spread out onto an aluminum cookie sheet. Digestion generally followed USEPA Method 3050B with the following exceptions. Two grams of material were used for digestion and these subsamples were prepared by collecting 20 increments from the spread out material. Analysis was performed by ICP-OES using USEPA Method 6010. The data from each of the three sampling approaches are summarized in Table 12 with the raw data provided in Appendix A, Table A2.

The results for only Zn, Pb, Sb, and Cu were evaluated in depth as these metals are typically the major constituents of small arms ammunitions. Studies conducted to compare the grid-node discrete sampling technique with the MI methodology indicate that the MI approach significantly improved the quality of the Pb and Sb data. Observations for Pb and Sb are similar and indicate MI sampling followed by milling the samples in the laboratory with the puck mill normalizes the distribution, produces much smaller variances, and tends to increase mean/median concentrations relative to grab samples.

The differences (e.g., as measured by central tendency and dispersion) between the grab and incremental data sets are not very notable for Zn. All of the Zn data sets were normal. A statistical difference was identified for the Zn medians but it is not clear the difference is of practical significance; m_1 (the median for the set of grab samples) is only somewhat smaller than m_{100} (the median of the set of MI samples prepared from 100 increments each) but $m_1 \approx m_{30}$ and m_{50} (Table 12). Similarly, a statistical difference was identified for the variances; the standard deviation s_1 (for the grabs) is numerically larger than the standard deviations for the incremental data sets. However, as $s_1 \approx s_{100} > s_{30}$ and s_{50} , it does not appear this finding is of practical significance. On the basis of these results it appears that the incremental sampling approach did not significantly improve the quality of the Zn results. It is suspected that significant differences between the grab and incremental data sets were not observed because the soil samples contained little or no metallic particles composed of Zn (e.g., brass casing fragments).

The incremental sampling approach did not seem to normalize the data or decrease their variability for Cu. A significant difference was not observed for the variances at the 95% level of confidence using Levene's test. How-

ever, the median Cu concentrations for the incremental sampling data sets were about 50–100% larger than the median for the grab data set. It appears that the MI approach produced larger average Cu concentrations; however, it is not clear if this is attributable to cross-contamination from the puck mill or increasing the surface area of the soil sample.

Table 12. Statistical analysis summary for antimony, copper, lead, and zinc.

Metal	k^1	n^2	Normal ³	KW ⁴	Levene's ⁵
Cu	1	30	Y	$p = 0.000$ $m_{100}, m_{50}, m_{30} > m_1$	$p = 0.172$ No difference
	30	7	N		
	50	7	Y		
	100	7	Y		
Pb	1	30	N	$p = 0.024$ $m_{100}, m_{50}, m_{30} > m_1$	$p = 0.000$ $S_1 > S_{30}, S_{50}, S_{100}$
	30	7	Y		
	50	7	Y		
	100	7	Y		
Sb	1	30	N	$p = 0.121$ $m_{100}, m_{50}, m_{30} > m_1$	$p = 0.014$ $S_1 > S_{30}, S_{50}, S_{100}$
	30	7	Y		
	50	7	Y		
	100	7	Y		
Zn	1	30	Y	$p = 0.047$ $m_{100} > m_1, m_{30}, m_{50}$	$p = 0.026$ $S_1 > S_{30}, S_{50}, S_{100}$ but $S_1 \approx S_{100}$
	30	7	Y		
	50	7	Y		
	100	7	Y		

1. k = number of increments per sample; for grabs $k = 1$.

2. n = number of replicates per DU.

3. N = Not normal at 95% confidence level of confidence; Y = normality assumption not rejected.

4. KW = two-tailed Kruskal-Wallis test p-value. m_k = median of data set with k increments. At least one median different with 95% confidence if $p \leq 0.05$.

5. Levene's test for variances; p-values. At least one variance different with 95% confidence if $p \leq 0.05$. s_k denotes standard deviation of data set with k increments.

The grab sample RSDs for the metals of interest (Sb, Cu, Pb, and Zn) are generally greater than our performance criterion of < 30% (Table 13). The grab sample RSDs for Sb, Cu, Pb, and Zn are 427, 44, 285, and 27%, respectively. Although, the RSDs for Cu and Zn are acceptable (25 and 9%, respectively) for the biased grab sample they are not for Sb and Pb (74 and 62%, respectively). In contrast, the RSDs for Sb, Cu, Pb, and Zn for the MI samples are < 30%. These results indicate estimates of the mean using grab samples will possess significant uncertainty. This is evident when comparing the grab samples collected with the grid-node approach to the biased grab samples. The biased grab samples were collected in locations

where the highest contaminant levels were expected. However, the mean and maximum values for Sb, Cu, Pb, and Zn for the biased grab samples were substantially lower than the mean and maximum values for the grabs collected using the grid node approach (Table 13).

Table 13. Grab samples from systematic-random sampling, biased grab samples and MI samples.

Test type	Mass (g)	Concentration (mg/kg)																
		Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	W	Zn
Grabs systematic sampling																		
n	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Mean	144	4219	20.0	0.760	7.40	6.22	300	12381	1976	197	9.91	710	5060	87.8	12.9	11.2	0.799	66.1
Median	146	4231	17.4	0.735	7.44	6.19	270	12380	1967	195	10.0	722	1238	10.0	12.1	11.2	0.745	61.9
Min	122	3784	15.7	0.620	6.31	5.58	69.8	9975	1748	175	8.67	468	43.9	0.898	9.86	9.14	0.400	35.8
Max	159	4577	39.5	1.13	8.38	6.99	598	14700	2325	242	10.7	1043	79020	2072	22.8	15.4	1.37	111
STD	10.1	158	5.61	0.104	0.486	0.409	132	797	124	15.4	0.439	116	14438	375	2.72	1.17	0.266	17.6
RSD (%)	7	4	28	14	7	7	44	6	6	8	4	16	285	427	21	10	33	27
Grabs biased																		
n	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
Mean	149	4161	16.2	0.647	6.97	5.85	269	11602	1899	188	9.33	692	1161	10.9	11.9	10.0	0.658	59.4
Median	149	4158	16.0	0.590	6.87	5.77	250	11375	1928	185	9.11	726	1103	8.79	12.0	10.0	0.655	59.4
Min	139	3968	14.6	0.520	6.56	5.20	216	10800	1734	173	8.74	532	479	3.48	10.1	8.75	0.510	52.1
Max	156	4412	17.9	0.960	7.47	6.86	392	13180	2062	207	10.5	816	1930	24.1	14.3	12.4	0.800	67.0
STD	6.17	150	1.29	0.158	0.322	0.570	65.9	863	115	13.3	0.658	129	718	8.15	1.48	1.32	0.093	5.53
RSD (%)	4	4	8	24	5	10	25	7	6	7	7	19	62	74	12	13	14	9
Multi-increment 100																		
n	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Mean	1539	6453	31.3	0.963	9.39	296	648	18242	2191	245	12.7	757	2929	22.8	25.3	16.6	0.256	81.8
Median	1419	6420	30.7	0.965	9.33	288	609	18390	2192	246	12.8	755	2638	20.7	25.5	16.7	0.250	78.2
Min	1177	6155	29.8	0.940	9.10	276	413	16980	2131	236	12.4	736	2490	19.5	24.3	16.0	0.140	65.2
Max	1992	6745	33.7	0.985	9.63	338	882	19200	2243	254	13.2	779	3595	28.9	26.7	17.3	0.420	95.9
STD	301	192	1.47	0.016	0.195	21.5	169	742	34.0	5.46	0.309	14.0	490	3.79	0.928	0.513	0.097	12.1
RSD (%)	20	3	5	2	2	7	26	4	2	2	2	2	17	17	4	3	38	15
n – sample size, Min – minimum, Max – maximum, RSD – relative standard deviation, STD – standard deviation Highlighted text indicates known contaminants of interest present																		

If the means of all the MI and grab samples for the project are compared, and the MI mean is assumed to be the more accurate estimate of the DU mean, it is evident that the grab samples either over or under estimate the DU mean (Table 14). In the case of Cu and Zn, the grab samples under estimate the mean, whereas the gridded grab sample over estimates the mean for Sb and Pb. Surprisingly, the biased grab sample under estimated

of the mean values for Sb and Pb. Even the naturally derived metals concentrations are under estimated with the grab sample as compared with MI samples consisting of 30 or more increments.

Table 14. Mean metal concentrations (mg/kg) for MI and grab samples.

Type	n	Mean concentration (mg/kg)															
		Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	Zn
Grab	30	4219	20.0	0.76	7.40	6.22	300	12381	1976	197	9.91	710	5060	87.8	12.9	11.2	66.1
Bias	6	4161	16.2	0.65	6.97	5.85	269	11602	1899	188	9.33	692	1161	10.9	11.9	10.0	59.4
MI-5	7	6230	29.1	1.16	8.85	262	539	17084	2088	220	12.4	727	2989	23.5	24.2	15.9	79.7
MI-10	7	4240	16.3	0.75	6.64	6.08	1277	12382	1987	192	9.30	721	2132	18.5	12.5	10.1	193
MI-20	7	5824	29.9	0.88	8.12	220	473	15005	2270	235	13.2	712	2689	23.1	17.9	14.3	80.7
MI-30	7	7224	31.2	1.30	9.56	395	573	17435	1992	228	13.5	792	2664	22.7	26.4	18.6	67.6
MI-50	7	6604	30.2	1.19	9.15	341	457	15946	2021	222	13.1	737	2156	17.6	23.1	16.9	67.2
MI-100	7	6453	31.3	0.96	9.39	296	648	18242	2191	245	12.7	757	2929	22.8	25.3	16.6	81.8
MI-200	1	5816	30.0	1.83	8.58	223	550	16752	2125	225	12.2	611	2717	22.6	22.0	15.2	77.2

MI – multi-increment sample, Highlighted text indicates known contaminants of interest present

4.3 Number of increments per decision unit

One of the questions of performing MI sampling is how many increments are needed per sample. Although this issue is likely to be site specific for the activity taking place and soil type, samples were collected to assess this issue for the small arms range at Camp Ethan Allen. Soil samples from the berm face DU were collected and consisted of 5, 10, 20, 30, 50, and 100 increments. Seven field replicate samples were collected for each increment value evaluated. The sampling and sample preparation methodology is discussed in Section 3.3. Briefly the soil samples were collected using systematic random sampling from the same DU discussed in Section 4.3 using the CMIST sampler. After collection using a 1-in. (2.54-cm) corer, the soil samples were air-dried, sieved, ground and then digested following USEPA Method 3050B with several modifications. Two gram subsamples, each prepared from 20 increments of ground material, were digested and subsequently analyzed using USEPA Method 6010.

A sampling error of < 30 % was achieved when the number of increments exceeded 30 (Table 15), with the exception of W for the 100-increment sample. Although, tungsten was analyzed, a special digestion approach was not used, which Clausen et al. 2007 demonstrated was necessary to achieve acceptable recoveries. Therefore, the tungsten results are not presented. It was hypothesized that the RSD will, in general, decrease as the

number of increments is increased. However, the RSDs did consistently decrease with increasing number of increments. The inconsistency is attributed to the small number of replicate samples that were collected (n is only seven). To see obvious trends and to conduct statistical tests for difference in population, the number of replicate samples preferred is closer to 30. However, it was not practical to collect 30 replicates for each increment value being evaluated.

The mean concentrations of the individual increment populations varied and did not systematically increase or decrease with increasing or decreasing number of increment (Table 14). For example, the highest mean Cu value occurred with the 10-increment sample whereas the lowest mean value was observed with the 20-increment sample (Table 14) (which was still significantly higher than either of the grab samples). The expectation based on observations of working with energetic contaminated soil was that the mean contaminant concentration would increase with number of increments collected and stabilize at some increment threshold. Again, this is likely a function of the number of replicate samples collected per population, i.e., seven, and likely could be ameliorated if closer to 30 replicate samples had been collected per population. Also, concentrations, detection limits, and distribution have an effect on how good the data can possibly be.

For comparison, the 200-increment samples results are included in Tables 14 and 15. Only a single 200-increment sample was collected; however, 30 laboratory replicates were collected and analyzed. Thus, for Table 15, the reported RSD is for 30 laboratory replicates, whereas the remainder of results for this table represents an analysis of seven different field replicates (laboratory replicates were excluded in generating the statistical values). It is likely that the mean metal values for the 200-increment sample is nearest to the “true” mean of the small arms range berm DU.

Table 15. Percent relative standard deviations (RSD) for MI samples with varying number of increments collected.

k	Percent relative standard deviation (RSD)															
	Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	Zn
5	3	4	7	4	10	22	4	4	4	3	10	25	25	31	6	9
10	8	5	26	3	6	162	4	1	4	4	16	32	63	10	5	154
20	27	49	34	22	121	26	22	8	18	26	4	30	50	33	32	15
30	3	3	7	4	7	15	10	2	4	3	6	14	15	5	6	6
50	3	7	4	3	15	21	10	1	2	4	4	11	11	6	6	10
100	3	5	2	2	7	26	4	2	2	2	2	17	17	4	3	15
200	6	7	2	2	3	18	4	6	5	2	4	4	7	7	1	11
k = number of increments per MI sample, Highlighted text indicates known contaminants of interest present																

A statistical summary of field replicate results by increment population is provided in Table 15 with all of the data provided in Appendix A, Table A3. Table 16 provides a statistical summary of the 200-increment laboratory replicate results where 30 samples were analyzed.

Table 15. Descriptive statistics for replicate MI samples by the number of increments collected.

k	Statistic	Concentration (mg/kg)															
		Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	Zn
5	n	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
	Mean	6230	29.1	1.16	9	262	539	1708	2088	220	12.4	727	2989	23.5	24.2	15.9	79.7
	Medi	6155	28.6	1.11	8.81	247	535	1695	2065	220	12.3	721	2797	21.1	21.0	15.7	83.2
	Min	6040	27.7	1.08	8.42	235	323	1647	1990	208	12.0	593	2284	16.8	20.2	14.4	65.5
	Max	6485	30.7	1.27	9.41	290	650	1797	2196	234	13.1	814	4187	34.2	41.1	17.4	85.9
	STD	166	1.11	0.08	0.33	25.4	120	638	75.0	9.22	0.38	72.7	754	5.99	7.60	1.01	7.41
	RSD	3	4	7	4	10	22	4	4	4	3	10	25	25	31	6	9
10	n	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
	Mean	4240	16.3	0.74	6.64	6.08	1277	1238	1987	192	9.30	721	2132	18.5	12.5	10.1	193
	Medi	4383	16.4	0.68	6.61	5.87	448	1252	1996	190	9.23	749	2103	15.5	12.8	9.9	77.8
	Min	3673	15.2	0.57	6.33	5.77	287	1146	1931	180	8.82	563	1334	8.08	10.7	9.5	63.4
	Max	4619	17.7	1.04	6.97	6.64	5930	1313	2016	201	9.83	827	3067	41.5	14.6	11.0	865
	STD	351	0.75	0.19	0.19	0.34	2064	542	29.1	7.24	0.33	112	679	11.6	1.27	0.48	297
	RSD	8	5	26	3	6	162	4	1	4	4	16	32	63	10	5	154
20	n	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
	Mean	5824	29.9	0.87	8.12	220	473	1500	2270	235	13.2	712	2689	23.1	17.9	14.3	80.7
	Medi	4667	19.1	0.67	6.79	22.4	431	1287	2142	211	14.5	713	2762	21.6	13.6	11.0	76.5
	Min	4465	17.5	0.60	6.47	6.20	330	1171	2103	195	9.44	682	1103	5.83	12.8	10.1	66.3
	Max	7640	47.1	1.23	10.3	573	689	1913	2521	287	17.5	741	3587	43.6	24.9	19.7	97.4
	STD	1550	14.6	0.29	1.81	266	123	3249	187	42.5	3.47	27.4	820	11.5	5.85	4.64	12.1
	RSD	27	49	34	22	121	26	22	8	18	26	4	30	50	33	32	15
30	n	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
	Mean	7224	31.2	1.30	9.56	395	573	1743	1992	228	13.5	792	2664	22.7	26.4	18.6	67.6
	Medi	7160	31.4	1.28	9.43	390	554	1698	1978	224	13.7	768	2728	23.5	26.3	17.9	67.8
	Min	6960	29.6	1.18	9.15	345	518	1519	1940	220	12.9	742	1993	17.5	24.8	17.5	60.5
	Max	7510	32.4	1.41	9.94	442	763	2040	2036	240	14.0	847	3122	26.7	28.2	20.2	73.1
	STD	228	0.86	0.08	0.34	29.0	85.1	1744	34.3	8.58	0.36	44.4	367	3.33	1.28	1.13	3.97
	RSD	3	3	7	4	7	15	10	2	4	3	6	14	15	5	6	6
50	n	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
	Mean	6604	30.2	1.19	9.15	341	457	1594	2021	222	13.1	737	2156	17.6	23.1	16.9	67.2
	Medi	6695	30.6	1.18	9.12	361	431	1516	2026	223	13.0	735	2037	17.0	22.9	17.0	65.5
	Min	6130	26.0	1.15	8.73	228	349	1446	1995	216	12.1	689	1835	15.0	21.5	15.4	58.2
	Max	6790	32.0	1.29	9.74	373	583	1796	2050	227	13.7	783	2447	20.5	25.5	18.7	76.5
	STD	229	2.01	0.04	0.30	51.6	95.8	1549	18.4	3.44	0.52	32.1	243	1.87	1.36	0.99	6.54
	RSD	3	7	4	3	15	21	10	1	2	4	4	11	11	6	6	10

k	Statistic	Concentration (mg/kg)															
		Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	Zn
100	n	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
	Mean	6453	31.3	0.96	9.39	296	648	1824	2191	245	12.7	757	2929	22.8	25.3	16.6	81.8
	Medi	6420	30.7	0.97	9.33	288	609	1839	2192	246	12.8	755	2638	20.7	25.5	16.7	78.2
	Min	6155	29.8	0.94	9.10	276	413	1698	2131	236	12.4	736	2490	19.5	24.3	16.0	65.2
	Max	6745	33.7	0.99	9.63	338	882	1920	2243	254	13.2	779	3595	28.9	26.7	17.3	95.9
	STD	192	1.47	0.01	0.19	21.5	169	742	34.0	5.46	0.30	14.0	490	3.79	0.92	0.51	12.1
	RSD	3	5	2	2	7	26	4	2	2	2	2	17	17	4	3	15

k = number of increments, Min – minimum, Max – maximum, n – number, ND – not detected. RSD – relative standard deviation,
Highlighted text indicates known contaminants of interest present

Table 16. Summary of results for 30 laboratory replicates for the 200-increment sample.

Statistic		Concentration (mg/kg)														
	Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	Zn
<i>n</i>	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Mean	11631	60.0	3.66	17.2	446	1100	33504	4250	450	24.4	1221	5433	45.1	44.1	30.4	15
Median	11690	60.1	3.64	17.1	447	1064	33840	4264	450	24.3	1221	5485	46.0	44.2	30.3	151
Min	11165	55.3	3.56	16.8	436	877	30305	4046	430	23.9	1185	4949	39.3	42.0	29.5	13
Max	12415	65.3	3.81	17.6	457	1449	35335	4390	463	25.3	1265	5724	50.5	47.4	31.1	18
STD	334	2.69	0.069	0.218	6.46	172	1243	95.7	9.30	0.326	23.4	224	2.73	1.45	0.458	15.
RSD (%)	3	4	2	1	1	16	4	2	2	1	2	4	6	3	2	10
n – number, Min – minimum, Max – maximum, RSD – relative standard deviation, ND – not detected. Highlighted text indicates known contaminants of interest present,																

4.4 Field splitting

Experiment 4 evaluated the appropriateness of field splitting to potentially reduce the volume of soil removed from the field and brought back to the laboratory. For this experiment and all subsequent experiments, the soil used was obtained by sampling Range 4-3 using systematic-random sampling; a 4-in.-diameter CMIST corer was used to collect 200-increments from 0 to 2 in., resulting in a 20-kg MI soil sample. The sample was sent to CRREL and divided into 12 splits using a rotary splitter. Six of the 12 splits were recombined for this experiment. (The remaining six splits were set aside.) The recombined material was split into four fractions using cone-and-quartering. The splits were subsequently processed as discussed in Section 3.4; the same approach used in Experiment #3 (see Section 4.3). Except, that after grinding of each quarter fractions, 10 laboratory replicates were collected, processed, and analyzed (Table 17). This resulted in 4 sets of 10 replicates for each metal for statistical comparisons.

Table 17 presents a summary of the results for the 10 replicates for each quarter fraction; all of the results are shown in Appendix A, Table A4. To assess whether cone-and-quartering is an appropriate technique, the mean and median metal concentrations of the four quarters were statistically compared for each of the small arms metals Sb, Cu, Pb, and Zn. As all of the data sets are not normal or lognormal, the non-parametric Kruskal-Wallis (KW) test was used to compare the four cone-and-quartering data sets for each metal. Statistically significant differences at well over the 99% level of confidence were observed for all four metals. The Pb and Sb medians differ by a factor of about 2. The results are summarized in Table 18 and suggest that cone and quartering does generally result in splits of comparable concentrations.

Table 17. Summary of metal results for the cone-and-quartering experiment.

Concentration (mg/kg)																
	Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	Zn
Quarter 1																
n	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Mean	5863	29.0	0.573	7.87	194	450	E	2144	223	10.9	665	3295	25.7	19.9	15.8	73.9
Median	5698	29.3	0.525	7.81	193	421	E	2184	227	10.8	631	3216	25.8	19.1	15.8	73.4
Min	5480	26.7	0.500	7.66	187	366	E	1946	203	10.5	625	3011	21.8	18.1	15.2	60.2
Max	6725	30.6	0.940	8.64	206	658	E	2262	235	11.6	802	3614	28.8	23.5	16.5	107
STD	435	1.31	0.132	0.286	6	87	E	110	11.3	0.365	61.4	213	2.17	1.87	0.380	13.2
RSD (%)	7	5	23	4	3	19	E	5	5	3	9	6	8	9	2	18
Quarter 2																
n	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Mean	6111	27.9	0.739	7.71	172	345	10801	2224	224	10.5	728	1447	10.0	20.4	14.8	60.8
Median	6078	26.8	0.858	7.74	172	340	10648	2079	211	10.3	764	1420	9.5	20.6	14.7	59.2
Min	5500	24.8	0.490	7.29	161	303	10370	2036	201	9.83	563	1198	8.37	18.1	14.1	57.3
Max	6580	41.4	0.925	8.41	188	398	12195	3492	351	12.1	863	1756	12.7	22.1	15.9	71.2
STD	305	4.90	0.203	0.329	6.81	26	513	447	45	0.615	116	163	1.49	1.07	0.501	4.00
RSD (%)	5	18	27	4	4	7	5	20	20	6	16	11	15	5	3	7
Quarter 3																
n	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Mean	6687	26.1	0.910	7.92	177	467	15492	2080	207	10.6	988	1281	8.67	22.3	14.8	62.6
Median	6750	26.0	0.910	7.91	177	443	16538	2078	206	10.6	989	1264	8.71	22.6	14.9	60.9
Min	6440	24.8	0.900	7.82	174	368	10430	2023	201	10.4	868	1216	7.89	21.3	14.1	56.7
Max	6860	28.0	0.920	8.10	180	587	17175	2145	218	10.8	1073	1369	9.34	23.0	15.1	71.3
STD	160	0.924	0.007	0.083	2.08	73.5	2162	31.6	4.46	0.090	59.1	58.5	0.461	0.623	0.339	4.54
RSD (%)	2	4	1	1	1	16	14	2	2	1	6	5	5	3	2	7
Quarter 4																
n	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Mean	6826	23.9	0.97	7.97	175	674	17155	2054	203	10.8	1253	3137	26.1	22.8	15.2	77
Median	6798	23.7	0.965	7.96	175	547	17680	2057	203	10.9	1254	3123	26.1	22.7	15.1	65.7
Min	6605	22.6	0.937	7.84	167	454	15180	2011	199	10.6	1193	2856	22.7	22.0	14.6	60.1
Max	7075	25.2	1.00	8.10	180	1190	17960	2085	206	11.0	1320	3505	29.2	23.8	15.8	120
STD	154	0.763	0.018	0.088	3.67	266	918	19.9	2.31	0.106	42.1	195	2.09	0.620	0.433	21.9
RSD (%)	2	3	2	1	2	39	5	1	1	1	3	6	8	3	3	29
E – error result outside calibration range, n – number, Min – minimum, Max – maximum, ND – not detected, RSD – percent relative standard deviation, STD – standard deviation																
Highlighted text indicates known contaminants of interest present.																

Table 18. Statistical evaluation for the cone-and-quartering experiment using the KW test.

Metal	Group*	Median (mg/kg)	p-value for KW test
Cu	1	421	0.000
	2	340	
	3	443	
	4	547	
Pb	1	3220	0.000
	2	1420	
	3	1260	
	4	3120	
Sb	1	25.8	0.000
	2	9.55	
	3	8.71	
	4	26.1	
Zn	1	73.4	0.004
	2	59.2	
	3	60.9	
	4	65.7	

*Each group consists of n=30 laboratory subsamples

4.5 Sample pulverization

One of the questions raised about the MI sample methodology is whether milling is necessary when the soil samples contain metal residues. To investigate this, laboratory replicates from an unground MI soil sample were compared with replicates from the same soil sample after it was milled.

The soil used for this experiment consists of the six splits that were set aside in Section 4.4. One of the splits was sieved with a no. 10 mesh sieve (the > 2mm fraction was set aside). One set of 15 laboratory replicates was obtained from the < 2 mm material by collecting 20 increment subsamples. The < 2-mm material was then milled using the puck mill at CRREL. Two sets of 15 replicate were then prepared from the ground material. Each replicate was prepared from 20 increments to build 2-g aliquots for digestion. The remainder of the sample preparation, digestion, and analysis procedures are the same as previously discussed in Sections 3.5 and 4.4.

The two ground sets of replicates were compared with one another as a “cross check” for the reproducibility of the ground results. The means and

variances of the two data sets were statistically compared. As expected, statistically significant differences between the variances were not detected at the 95% level of confidence using Levene's test for any of the four metals. Statistically significant differences for the medians were observed for Cu, Sb, and Zn at the 95% level of confidence using the KW test. However, these differences did not appear to be of practical significance; the medians differed by no more than 15%, which is within the typical tolerance for laboratory analytical error for the metal analyses.

In contrast, large differences were observed between the ground and unground data sets for variances and medians. Statistically significant differences for the Pb and Sb variances were observed at well over the 99% level of confidence using Levene's test. The Pb and Sb standard deviation of the unground results was over five times larger than the standard deviations of the ground results. Similarly, although the median Pb and Sb concentrations of the two sets of ground samples were very similar, they were twice as large as the median Pb and Sb concentrations of the unground samples. This is very visually apparent from the box and whisker plots for Pb shown in Figure 10. The medians and interquartile ranges (IQRs) for the two ground data ("Ground-1" "Ground-2") are very similar. The interquartile range (the "length of the box") is a measure of variability (e.g., like the standard deviation); it is an interval in which the middle 50% of the results fall. The IQR of the unground data set is much larger than the IQRs of the two ground data sets. The medians of the ground data sets are also significantly larger than the medians of the unground data sets. The box and whisker plots also indicate that the distribution of the unground results is very positively skewed (e.g., there is a large outlier between 3000–3500 mg/kg). In contrast, the distributions of the ground results are relatively symmetrical (e.g., may be approximately normal).

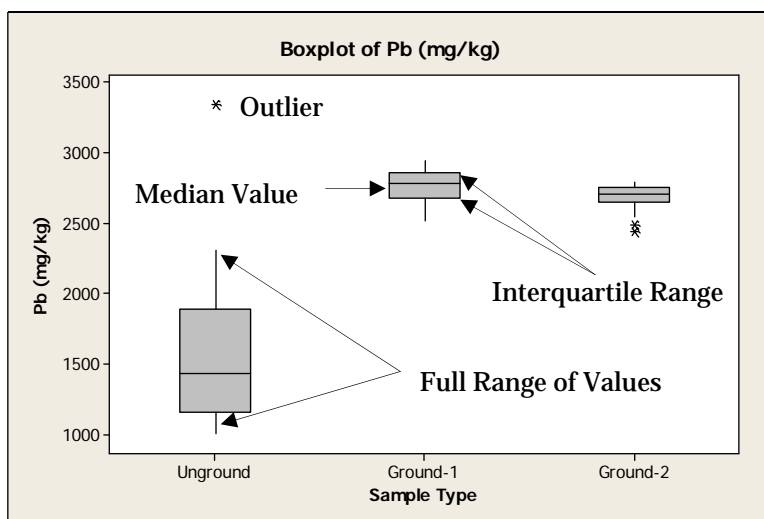


Figure 10. Box and whisker plots of lead (mg/kg) for the unground and puck mill ground samples.

Statistically significant differences between the variances of the ground and unground results were not observed at the 95% level of confidence using Levene's test for Cu and Zn, but the unground Zn and Cu medians were consistently smaller than the ground Zn and Cu medians. The unground Cu median was about 30-40% smaller than the ground medians. The unground and ground means were within about 15% of one another.

From the RSDs for the unground and ground laboratory replicates samples, it is apparent that all of the ground samples met our target of 15% (Table 19). In contrast, the RSDs of the unground replicates for Sb, Cu, Pb, and Zn (the constituents of interest for small arms), generally exceed 15%. In all cases, the means for the ground results are larger than the means of the unground results (Table 19). A complete set of results for this experiment is provided in Appendix A, Table A5.

	Concentration (mg/kg)															
	Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	Zn
Unground																
<i>n</i>	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Mean	4124	17.1	1.08	6.48	6.12	357	9307	2018	201	9.09	559	1600	14.2	12.6	10.0	66.1
Median	4118	16.4	1.08	6.51	6.14	329	9325	2010	200	9.08	558	1432	10.9	12.7	10.0	63.7
Min	3954	15.2	1.04	6.26	5.72	312	9120	1983	197	8.85	548	1004	6.86	11.8	9.27	60.0
Max	4266	23.4	1.11	6.73	6.74	676	9455	2055	206	9.65	573	3340	44.3	13.7	10.8	107
STD	94.7	2.48	0.017	0.139	0.282	89.5	98.5	24.7	2.56	0.191	8.14	626	9.84	0.546	0.408	11.3
RSD (%)	2	15	2	2	5	25	1	1	1	2	1	39	69	4	4	17
Ground Group 1																
<i>n</i>	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Mean	5509	31.6	1.82	8.75	229	496	16676	2242	235	12.4	590	2760	21.8	20.6	15.2	81.0
Median	5505	31.5	1.82	8.75	230	492	16915	2255	235	12.4	589	2779	22.2	20.6	15.2	80.4
Min	5425	29.4	1.79	8.46	222	391	14775	2141	225	12.2	571	2509	18.9	20.1	14.7	67.0
Max	5615	34.8	1.86	8.94	236	636	17620	2290	240	12.6	610	2936	24.9	21.2	15.6	93.5
STD	57.6	1.31	0.024	0.110	4.52	74.3	700	41.1	4.00	0.098	10.3	120	1.45	0.323	0.230	7.79
RSD (%)	1	4	1	1	2	15	4	2	2	1	2	4	7	2	2	10
Ground Group 2																
<i>n</i>	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Mean	6123	28	1.8	8.4	217	605	16828	2008	215	12	631	2673	23	23	15	73
Median	6185	29	1.8	8.4	217	572	16925	2009	215	12	632	2706	24	24	15	71
Min	5740	26	1.8	8.3	214	486	15530	1905	205	12	615	2440	20	22	15	65
Max	6800	30	1.9	8.7	221	813	17715	2100	223	13	655	2788	26	26	16	93
STD	276	1.4	0.04	0.11	1.9	98	543	55	5.3	0.23	13	104	1.3	1.1	0.23	7.9
RSD (%)	5	5	2	1	1	16	3	3	2	2	2	4	5	5	2	11
n – number, Min – minimum, Max – maximum, ND – not detected, RSD – percent relative standard deviation, STD – standard deviation Highlighted text indicates known contaminants of interest present																

Table 21. Relative standard deviations (RSDs) of unground and ground splits processed with different milling equipment.

		Percent relative standard deviation (RSD)																			
Machine Type	Lab	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	K	Na	S	V	Zn
Unground 1	TA	4	5	NA	ND	5	5	257	4	NA	4	7	NA	61	116	NA	NA	NA	NA	4	162
Unground 2	CRREL	2	15	NA	2	2	5	25	1	1	1	2	1	39	69	4	NA	NA	NA	NA	17
Mortar & pestle	CRREL	5	5	NA	ND	4	4	39	4	4	3	3	5	32	55	11	NA	NA	NA	4	28
Puck mill 1	APPL	5	6	NA	ND	4	4	10	4	4	4	4	3	15	21	4	NA	NA	NA	5	5
Puck mill 2	CRREL	1	4	NA	1	1	2	15	4	2	2	1	2	4	7	2	NA	NA	NA	2	10
Puck mill 3	CRREL	5	5	NA	2	1	1	16	3	3	2	2	2	4	5	5	NA	NA	NA	2	11
Puck & ring mill	TA	6	6	5	ND	5	5	5	4	5	5	5	5	5	8	NA	6	6	7	5	6
Ball mill	TA	1	1	1	ND	1	1	3	1	1	1	1	2	1	8	NA	1	2	12	1	2
NA-not analyzed, ND – not detected, Bolded values > 15%, Highlighted text indicates known contaminants of interest present																					

Table 22. Mean concentrations (mg/kg) of unground splits and ground spits processed with various milling equipment.

Machine Type	Lab	Mean Concentration (mg/kg) ¹																				
		Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	K	Na	S	V	Zn	
Unground 1	TA	3538	11.9	NA	ND	4.37	4.47	1061	9173	NA	179	7.45	NA	2043	15.9	NA	NA	NA	NA	6.19	83.7	
Unground 2	CRREL	4124	17.1	NA	1.08	6.48	6.12	357	9307	2018	201	9.09	559	1600	14.2	12.6	NA	NA	NA	NA	66.1	
Mortar & pestle	CRREL	4173	17.3	NA	ND	6.31	6.26	372	13818	2025	184	8.37	596	1359	10.5	13.5	NA	NA	NA	10.3	71.5	
Puck mill 1	APPL	2930	14.6	NA	ND	4.25	108	279	7702	1520	142	6.46	335	3041	11.2	8.80	NA	NA	NA	5.72	49.9	
Puck mill 2	CRREL	5509	31.6	NA	1.82	8.75	229	496	16676	2242	235	12.4	590	2760	21.8	20.6	NA	NA	NA	15.2	81.0	
Puck mill 3	CRREL	6123	28.4	NA	1.84	8.42	217	605	16828	2008	215	11.9	631	2673	23.4	23.4	NA	NA	NA	15.2	73.3	
Puck & ring mill	TA	5707	40.6	3121	ND	6.92	353	346	14200	2144	221	13.2	384	2349	5.00	NA	1595	648	21.6	14.3	50.0	
Ball mill	TA	4983	31.9	2709	ND	6.00	9.37	319	17240	2212	226	9.38	427	1687	3.47	NA	1225	331	16.8	10.8	51.6	
¹Each population consists of 15 laboratory replicate samples. NA – not analyzed, ND – not detected, Highlighted text indicates known contaminants of interest present																						

Box and whisker plots for the Pb results are presented In Figure 11 for the sets of unground and ground replicates. The two sets of 15 replicates for CRREL puck mill were combined into single set of 30 replicates (denoted as “Puck-CRREL”) as the results were similar.

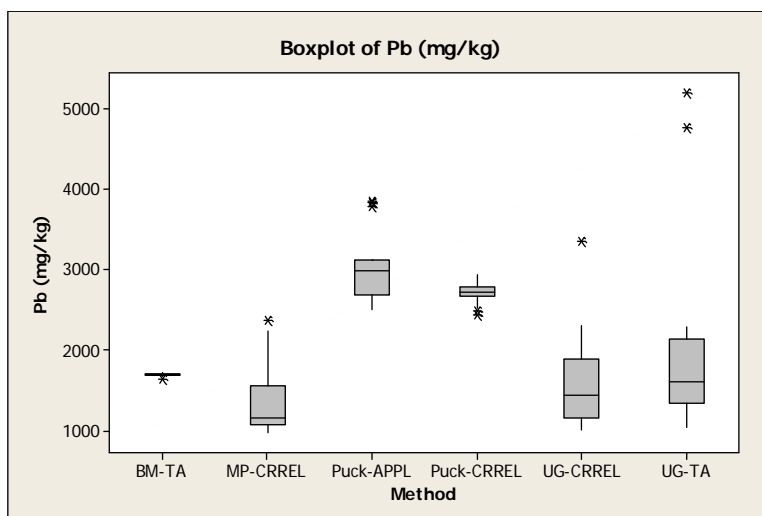


Figure 11. Box and whisker plots for lead by type of milling equipment. BM = ball mill, MP = mortar and pestle, Puck = puck and ring mill, UG = unground, TA = Test America

As shown by Figure 11, the two unground data sets exhibit similar variability and are positively skewed. Statistically significant differences between the variances of the two unground data sets were not detected by the Levene's test at the 95% level of confidence for Cu, Pb, Sb, or Zn. Figure 11 suggests that the variances of the two unground data sets are larger than the variances of the ground data sets, as the unground data sets exhibit larger outliers and IQRs. The variances of the ground data sets tended to differ from one another. When Levene's test was used to compare the variances of the ground data sets BM-TA ($n=15$), MP-CRREL ($n=15$), Puck-APPL ($n=15$), and Puck-CRREL ($n=30$), statistically significant differences at the 95% level of confidence were observed for all four metals. The ball mill data possessed the smallest variance for Cu, Pb, Sb, and Zn. The ball mill standard deviations were at least two to five times smaller than the standard deviations of the puck mill and mortar and pestle data. The puck mills tended to produce better precision than the mortar and pestle but this was not consistently so for all four metals. Generalization about the mortar and pestle and the puck mill were problematic, as the two puck mills did not consistently produce comparable results. When Levene's test was used to compare the puck mill variances at the 95% level of confidence, the Puck-APPL Cu and Zn variances were larger than Puck-TA Cu

and Zn variances, while the Puck-APPL Pb variance was smaller than the Puck TA Pb variance. However, in terms controlling sub-sampling variability, the overall performance for the various milling equipment seemed to be as follows: ball mill > puck mill > Mortar Pestle > No Milling

4.6.1 Mortar and pestle

A mortar and pestle was used to assess the utility of processing soil samples with this apparatus. USEPA Method 3050B indicates, if appropriate, the sample be milled with a mortar and pestle. However, it is our observation from discussions with various commercial analytical laboratories that the mortar and pestle is not used unless the client specifically specifies such use. The mortar and pestle consists of ceramic components. The metals cadmium and tungsten were analyzed but none were detected in any of the 15 laboratory replicate samples at a reporting limit of 0.16 mg/kg. A comparison of RSD for the unground to the mortar and pestle results indicates a reduced total sample error. However, the RSD for the mortar pestle results (Table 21) are still above our laboratory acceptance criteria of < 15% error. The total errors for Sb, Cu, Pb, and Zn are 55, 39, 32, and 28%, respectively.

The mean Sb and Pb values determined from use of the mortar and pestle (Table 23) sample were generally lower than the means for the unground samples (Tables 20 and 22).

Table 23. Descriptive statistics (mg/kg) for 15 replicates processed with the mortar and pestle.

	Mean Concentration (mg/kg)														
	Al	Ba	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	Zn
<i>n</i>	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Mean	4173	17.3	6.31	6.26	372	13818	2025	184	8.37	596	1359	10.5	13.5	10.3	71.5
Median	4111	17.4	6.37	6.27	329	14010	2032	185	8.41	598	1156	7.83	13.5	10.4	67.0
Min	3753	15.4	5.86	5.63	278	12665	1921	175	7.85	522	973	6.36	10.7	9.19	61.2
Max	4599	18.7	6.73	6.53	886	14470	2139	194	8.75	644	2371	26.7	16.9	10.7	142
STD	227	0.832	0.231	0.236	145	551	73.8	5.48	0.263	31.9	440	5.74	1.43	0.458	19.9
RSD (%)	5	5	4	4	39	4	4	3	3	5	32	55	11	4	28
n – number, Min – minimum, Max – maximum, RSD – percent relative standard deviation, STD – standard deviation Highlighted text indicates known contaminants of interest present															

4.6.2 Puck mill

Three splits were milled with the puck mill, with 15 replicates laboratory samples collected and analyzed. Two of the samples were processed using the puck mill at CRREL and one sample at APPL laboratories. In each case, the samples were processed using an interval of 5 × 60 s with 1 mi-

nute of cooling between grinding. The sample digestion procedures were identical, with the exception that hydrochloric acid (HCl) was not added to the samples digested at APPL or Test America. The APPL and Test America samples that were analyzed with an ICP-MS and USEPA Method 3050B do not include the use of HCl. In comparison, the CRREL samples were analyzed with an ICP-OES, which requires digestion with HCl.

As indicated in Table 21, the CRREL and APPL puck mill replicates met the 15% acceptance criterion for the %RSD with a few exceptions that marginally exceed the limit. Although all three splits originate from the same bulk 20-kg field sample, the mean values for all metals were consistently lower for the APPL results. The means of the two CRREL puck mill splits ground were similar. The difference between the CRREL and APPL results may be ascribable to difference in the digestion and instrumental analyses (e.g., the different acids used to digest the replicates prior to the ICP-MS and ICP-OES analyses).

Test America also processed a sample using a puck and ring mill. The RSDs for this population of samples is very comparable to the puck mill results (Table 21). The means for the Cu and Pb results between the TA puck and ring mill are comparable to the CRREL puck mill results (Table 22). The mean Sb and Zn results for the TA puck and ring mill were lower than the CRREL results but comparable to the APPL puck mill values.

4.6.3 Ball mill

Another milling apparatus, a ball mill, was used to process a separate split sample of the original 20-kg bulk material. The container of the ball mill is a polyethylene can and ceramic balls are used to grind the soil so no metallic components come in contact with it. Again, the same sample preparation and digestion procedures were used for the ball mill samples following the grind as were used with the puck mill. Because the samples for the ball mill were analyzed by ICP-MS, HCl was not added to the sample during digestion. Unlike the puck mill, the soil samples were processed in the ball mill for 18 hr as compared to 5×60 s for the puck mill. The calculated RSD for the ball mill population of samples was very good with values less than 15% for the analytes of interest (Table 21). However, one difference noted is that the mean values for Sb and Pb obtained with the ball mill were lower than the values obtained from processing the soil with the puck mill (Table 22). The Cu and Zn values were comparable between the two milling devices.

4.7 Milling interval

The results presented in Section 4.6 indicate that the puck mill and ball mill are appropriate milling equipment for reducing the total sampling error to acceptable levels. The selection of a milling interval of 5×60 s for the puck mill is based on guidelines provided in USEPA Method 8330B for energetics. Because propellants are present at the firing point of small arms ranges, a milling interval appropriate for both energetics and metals is desired. However, the shortest milling interval, to reduce the error associated with heterogenous samples, is desired to facilitate rapid sample throughput. Therefore, for the puck mill a study was conducted evaluating milling intervals of 30, 60, 90, 120, and 360 s. The milling intervals evaluated with the ball mill were 8, 12, 16, and 20 hr.

The same 200-increment reference soil previously discussed was used for all tests. The approach for each piece of milling equipment was to grind the soil for the shortest time interval, pull 15 laboratory replicates, and then grind the soil for the next time interval with the process repeated until the last time interval was achieved. The digestion and analysis procedures were identical for all samples and have been previously discussed. All of the sample results for this set of experiments are included in Appendix A, Table A7.

4.7.1 Puck mill

To compare the effectiveness of the different milling intervals, the RSDs for each time were calculated for the 15 replicate samples (Table 24). The time interval of 0 s represents the unground control sample. The results suggest a milling interval of 60 s might be sufficient; however, the population of data for Cu has a RSD of 31% at 90 seconds. Our target criterion for inter-sample comparisons is 15%. It seems that 120 s of milling with the puck mill is adequate to achieve RSDs of $< 15\%$, although the Cd seems anomalous given the low RSDs for all other time intervals. Clearly, the 5×60 s milling interval is successful in achieving a low total sample error.

Laboratory sub-sampling variability for Pb and Sb decreased overall as the puck mill grinding time was increased from 0 to 300 seconds. This is shown qualitatively in the scatter plots of the standard deviation of Pb and Sb versus time; these plots are similar in appearance. (Fig. 12 and 13).

Table 24. Percent relative standard deviations by different milling intervals with the puck mill.

Time (s)	Percent Relative Standard Deviation (RSD)															
	Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	Zn
0	2	15	2	2	5	25	1	1	1	2	1	39	69	4	4	17
30	7	7	5	5	6	10	5	6	4	4	5	36	55	8	3	7
60	4	3	3	2	2	20	3	2	2	3	2	12	18	12	3	12
90	7	7	4	3	5	31	5	7	7	4	4	10	15	31	5	18
120	10	13	35	2	2	20	19	11	8	4	6	12	18	17	4	10
300	4	1	1	2	15	4	2	2	1	2	4	7	2	2	ND	10

ND – not detected, s – seconds Bold values > 15%,
Highlighted text indicates known contaminants of interest present

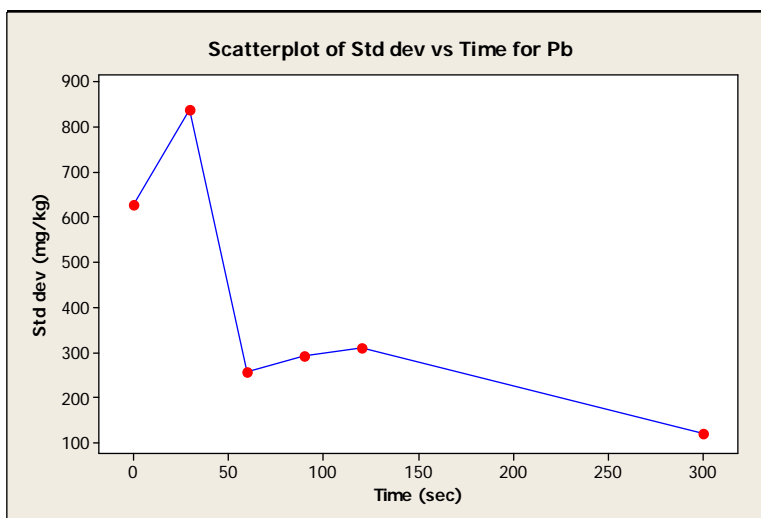


Figure 12. Scatter plot of the standard deviation of lead (mg/kg) versus the puck mill grinding time.

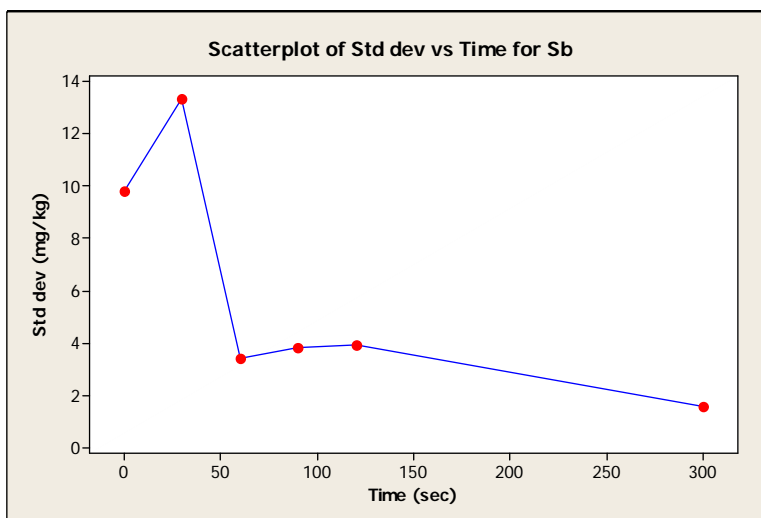


Figure 13. Scatter plot of the standard deviation (mg/kg) of antimony versus the puck mill grinding time.

The soil samples contained metallic fragments composed of Pb and Sb. Increasing the grinding time reduced the particle size of these fragments, resulting in corresponding decrease in fundamental errors.

However, there is no clear relationship between grinding time and the variability for Cu and Zn. The box and whisker plots shown below for Cu and Zn suggest that grinding for at least 120 s may be beneficial (Fig. 14 and 15). The IQRs of the Cu and Zn results tend to be variable and the distributions positively skewed when the grinding time is less than 120 s. Similarly, the Zn box and whisker plots exhibit large outliers when the grinding time is less than 120 s. In contrast, the Zn and Cu distributions the 120- and 300-s grinding times are relatively normal (the null hypothesis the distributions are normal is not rejected with 95% confidence); also, the variances of the results for 120- and 300-s grinding times are similar for both Cu and Zn (the null hypothesis that the variances are equal is not rejected with 95% confidence using either the F-test or Levene's test).

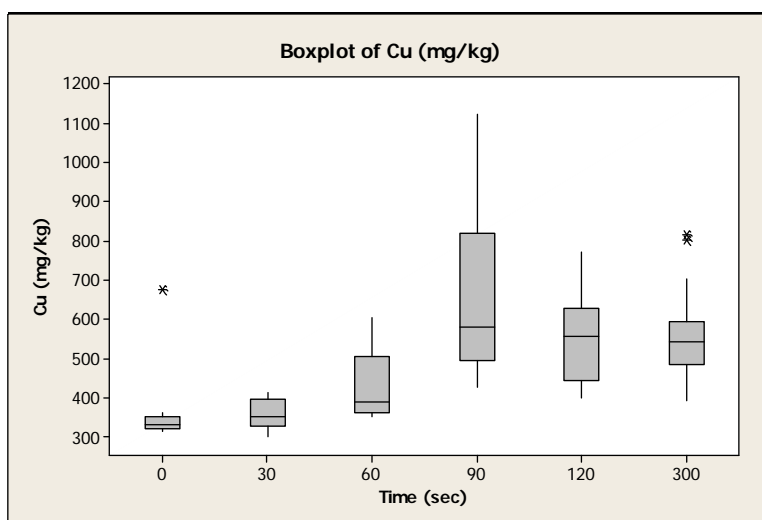


Figure 14. Box and whisker plots for copper (mg/kg) by puck mill grinding time.

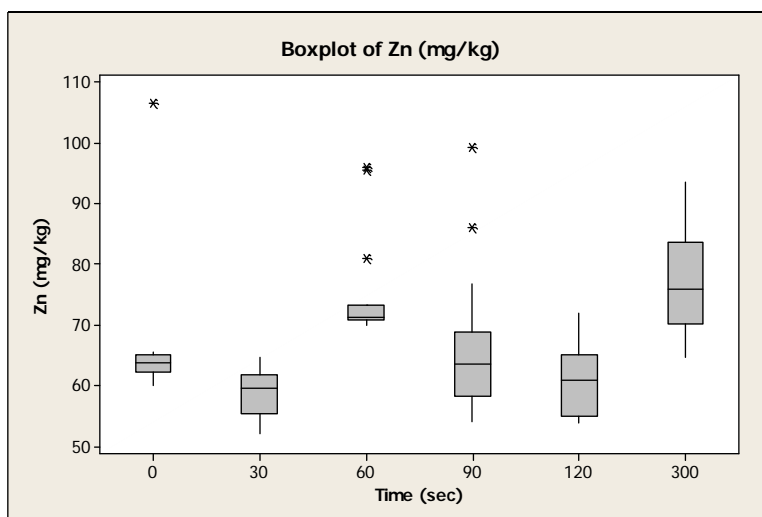


Figure 15. Box and whisker plots for zinc (mg/kg) by puck mill grinding time.

One of the questions of using a puck mill is how much does this change the metal results. Table 25 compares the mean values (mg/kg) for each of the metals by milling time. Fifteen laboratory replicate samples were analyzed for each time interval. Time zero represents the unground control sample. It is apparent that milling the soil samples with a puck mill composed of metallic components results in an increase in most metal concentrations, although there is enough variability in results that clear positive trends are not apparent for all metals.

Table 25. Comparison of mean values by different milling intervals (s) with the puck mill.

Time (s)	Concentration (mg/kg)															
	Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	Zn
0	4124	17.1	1.08	6.48	6.12	357	9307	2018	201	9.09	559	1600	14.2	12.6	9.99	66.1
30	4754	19.6	0.813	6.71	74.7	357	14344	1848	183	9.09	739	2348	24.2	18.4	12.0	58.6
60	5378	29.3	0.928	8.04	135	430	15597	2187	224	10.2	576	2187	18.6	18.7	14.1	75.1
90	6518	24.7	1.05	7.69	162	646	16933	1824	196	11.0	570	2818	24.8	19.9	15.0	66.7
120	7156	26.8	0.89	8.01	233	538	16653	1873	200	12.5	629	2562	21.6	27.2	15.6	60.8
360	5509	31.6	1.82	8.75	229	496	16676	2242	235	12.4	590	2760	21.8	20.6	15.2	81.0
% Change ¹	16	61	124	30	207	39	16	21	28	37	-20	18	-10	12	27	38

¹Percent change from 30 to 360 seconds of milling. NA – not analyzed, ND – not detected, s – seconds
 Blue highlighted text indicates known metal constituents present in the bowl and puck of the puck mill
 Yellow highlighted text indicates known contaminants of interest present and constituents present in the bowl and puck of the puck mill

As expected, metals that are major constituents of the puck mill grinding surfaces (e.g., Fe and Cr) tended to increase as the grinding time increased. This is clearly evident in box and whisker plots that are shown for

Fe and Cr (Fig. 16 and 17). The median Fe and Cr concentrations appear to increase with time and then “level” at about 120 s.

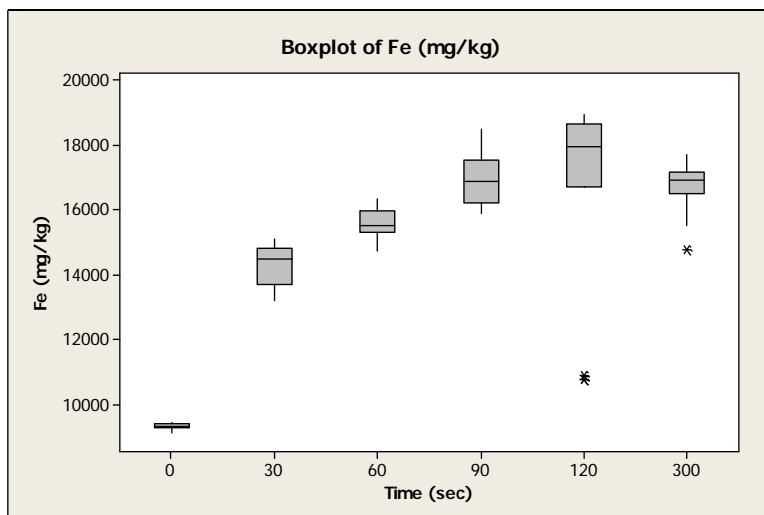


Figure 16. Box and whisker plots for iron (mg/kg) by puck mill grinding time.

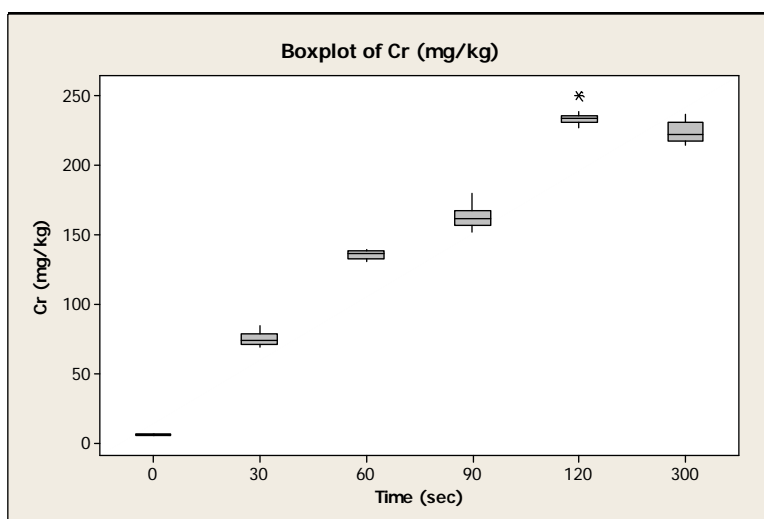


Figure 17. Box and whisker plots for chromium (mg/kg) by puck mill grinding time.

The metals Al, Mn, V, and Ni, which also are constituents of the puck mill, produce similar box and whisker plots (not shown) as Fe and Cr, though there was not a clear relationship between the grinding time and the median concentrations. The only appreciable increase in metal concentrations with grinding time for those metals known to be constituents of the puck and bowl was Cr (Table 25). In contrast, as shown by the box and whisker plots for Pb and Sb, the median Pb and Sb concentrations are not strongly

time dependent after the first 30 s of grinding (Fig. 18 and 19). Note that the puck mill contains no more than trace levels of these metals.

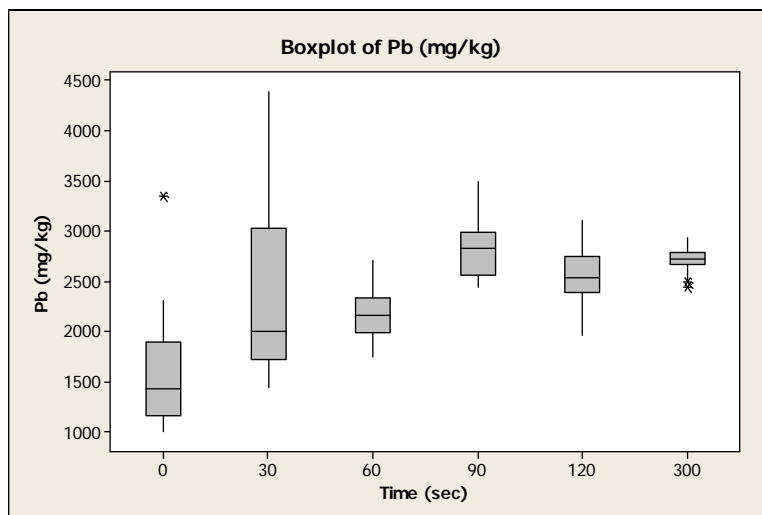


Figure 18. Box and whisker plots for lead (mg/kg) by puck mill grinding time.

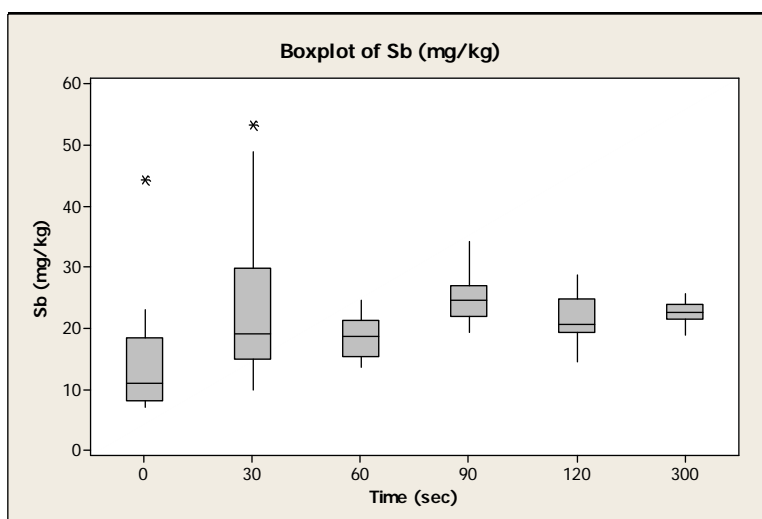


Figure 19. Box and whisker plots for antimony (mg/kg) by puck mill grinding time.

The relations between the grinding time and median Cu concentrations are not as apparent. The box and whisker plots for Cu suggest (not shown) that the median Cu concentrations initially increase then “level” at about 90 s. This is also consistent with the median and mean Cu concentration scatter plots versus grinding time (Fig. 20). Cu is present in the puck-mill grinding surfaces at concentrations of the order of 1000 mg/kg, but per the reasons discussed in Section 5, it does not appear that the increase in Cu is attributable to contamination from the puck mill. The box and

whisker plots for Zn (not shown), which is present in the puck mill at trace levels only, indicate that the median Zn concentration does not appear to be correlated with grinding time.

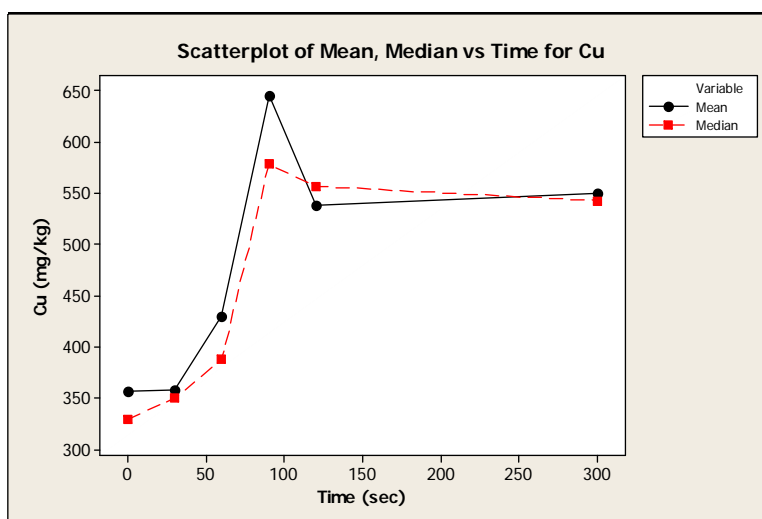


Figure 20. Scatter plots of the mean and median copper concentration (mg/kg) versus the puck mill grinding time.

4.7.2 Ball mill

Table 26 presents the RSD for each of the metals by the milling interval with the ball mill. The population of data for time zero represents the un-ground control. Our RSD target criterion of 15% was met for the metals of interest (Sb, Cu, Pb, and Zn) within 12 hours of milling with the ball mill.

Table 26. Comparison of percent RSD by different milling intervals with the ball mill.

Time (hr)	Percent relative standard deviation (RSD)												
	Al	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	V	Zn
0	5	NA	ND	5	5	257	4	4	7	61	116	NA	162
8	4	5	ND	3	9	4	8	2	4	13	23	8	8
12	5	10	ND	3	11	8	4	4	3	6	7	8	7
16	4	6	ND	1	6	6	2	2	1	6	14	5	3
20	4	6	ND	1	6	6	2	2	1	6	14	5	3

NA – not analyzed, ND – not detected, s – seconds

Highlighted text indicates known contaminants of interest present

As there are no metallic components exposed to the ball mill (ceramic balls with Teflon coated cans were used) the expectation is that the metal concentration should remain relatively constant with increasing milling time. However, the particular sample used in this experiment was an unsieved portion of the 20-kg bulk samples. Consequently, large chunks of metal

were present in the sample. This likely explains the observed metal concentration increase with increasing milling time (Table 27) as the particle size of the metal residue was reduced, thereby increasing the surface area of metal present. Visual observation of the samples, even after 20 hr of milling, showed visible metal particles present. It is likely that the metal concentrations would continue to increase until all of the metal has been reduced to a consistent particle size.

Table 27. Comparison of mean values by different milling intervals (hr) with the ball mill.

Time (hr)	Mean concentration (mg/kg)												
	Al	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Sb	V	Zn
0	3538	11.9	ND	4.37	4.47	1061	9173	179	7.45	2043	15.9	NA	83.7
8	4283	20.2	ND	4.75	6.48	1021	11564	199	8.17	4798	35.0	7.57	69.4
12	4589	22.4	ND	4.93	7.68	1040	13336	194	8.78	5810	46.1	8.64	80.1
16	4764	26.4	ND	4.80	9.33	1179	13850	203	8.65	6375	44.9	7.78	91.4
20	5058	29.2	ND	4.84	10.4	1314	NA	209	NA	7153	55.2	8.47	93.4
% Change ¹	18	45	ND	2	60	29	NA	5	NA	49	58	12	35

¹Percent change from 30 to 360 s of milling., NA – not analyzed, ND – not detected
 Highlighted text indicates known contaminants of interest present

4.8 Digestion mass

A study was done to determine if increasing the digestion mass reduces laboratory subsampling variability. Studies for energetic residues that were done by CRREL indicated that increasing the extraction mass from 2 g to 10 g reduced sub-sampling variability (Hewitt et al. 2009; Walsh et al. 2006a, 2002). As result, USEPA Method 8330B for energetics now stipulates an extraction mass of 10 g. The USEPA Method 3050B for metals digestion specifies digestions of a 0.5- to 2-g samples. Therefore, an experiment was done to assess method performance for 3050B for different soil to solution mass ratios. The study assessed digestion of 0.5-, 1-, 2-, 5-, and 10-g samples. The same 200-increment reference soil previously discussed was used for all tests. The same sample preparation, digestion, and analytical methods as discussed previously were used. The digestion mass was the only parameter that was varied. All of the results of the results for this study are included in Appendix A, Table A8. Tungsten was not detected in any of the samples for this experiment.

Some descriptive statistics for the set of replicates that were analyzed for each digestion mass are presented in Table 28. The %RSDs were generally less than 15% for Sb, Pb, and Zn for each set of replicate digestion masses.

There were some values marginally greater than 15% for Cu for the digestion masses of 0.5, 1, and 5 g; however, 2 and 10 g met the 15% criteria.

The box and whisker plots for Cu, Pb, Sb, and Zn (Fig. 21–24) suggest that, overall, the digestion mass does not strongly affect method performance.

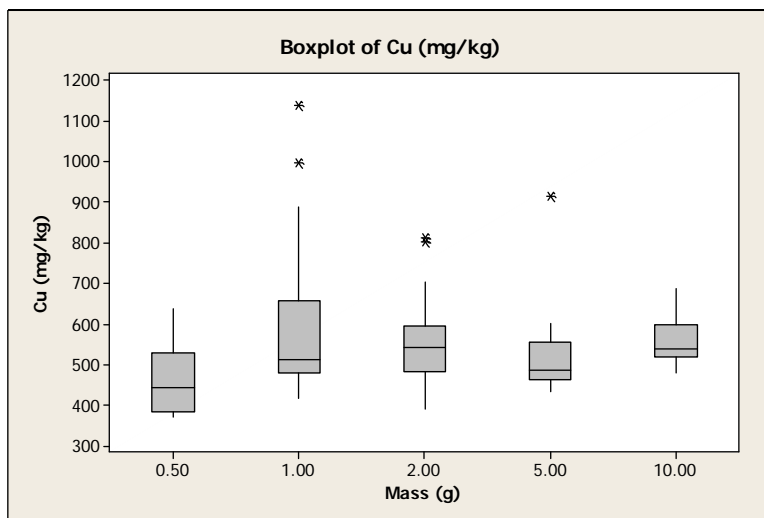


Figure 21. Box and whisker plots for copper by digested soil mass.

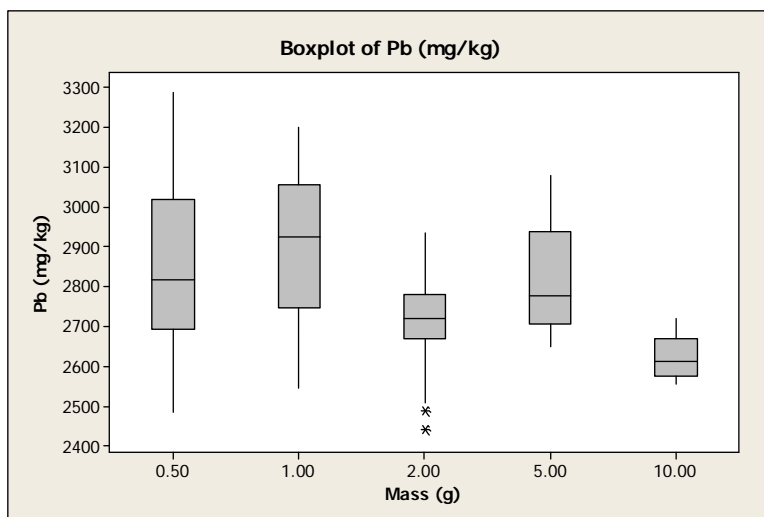


Figure 22. Box and whisker plots for lead by digested soil mass.

Table 28. Summary of metal results by different digestion mass of sample ground 5 × 60 s in puck mill.

	Concentration (mg/kg)															
	Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	Zn
Half gram sample																
<i>n</i>	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Mean	5116	28.6	0.96	8.55	219	466	15629	2120	229	11.2	725	2848	24.6	19.4	13.9	79.0
Median	5099	28.6	0.97	8.53	216	443	15560	2115	229	11.2	732	2816	23.6	19.5	13.8	77.7
Min	4827	25.7	0.93	8.32	210	370	14000	2047	221	10.5	688	2483	21.2	18.2	13.2	70.9
Max	5383	31.0	0.99	8.96	229	637	16590	2213	239	11.8	770	3287	30.6	20.6	15.0	100
STD	162	1.67	0.018	0.206	6.50	94.6	731	47.6	4.92	0.354	28.4	236	2.85	0.746	0.594	7.99
RSD (%)	3	6	2	2	3	20	5	2	2	3	4	8	12	4	4	10
One gram sample																
<i>n</i>	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Mean	5550	28.6	0.58	7.74	225	610	16851	2160	227	11.9	922	2913	23.3	21.2	14.6	83.4
Median	5610	28.8	0.58	7.74	225	511	16745	2173	226	11.9	914	2923	23.1	21.4	14.6	79.2
Min	5085	26.5	0.55	7.52	221	415	16040	2091	222	11.5	854	2545	18.9	19.1	13.6	70.4
Max	5916	30.1	0.61	8.02	230	1140	17680	2212	232	12.2	998	3202	28.3	23.2	15.3	112
STD	237	1.17	0.017	0.146	2.86	221	530	41.2	3.06	0.179	48.0	203	2.72	1.11	0.555	12.5
RSD (%)	4	4	3	2	1	36	3	2	1	2	5	7	12	5	4	15
Two gram sample																
<i>n</i>	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Mean	5816	30	2	9	223	550	16752	2125	225	12	611	2717	23	22	15	77
Median	5678	30	2	9	221	543	16920	2121	224	12	612	2718	23	22	15	76
Min	5425	26	2	8	214	391	14775	1905	205	12	571	2440	19	20	15	65
Max	6800	35	2	9	236	813	17715	2290	240	13	655	2936	26	26	16	94
STD	368.6	2.1	0.0	0.2	7.1	101.6	620.6	128.	11.1	0.3	23.9	118.7	1.6	1.6	0.2	8.7
RSD (%)	6	7	2	2	3	18	4	6	5	2	4	4	7	7	1	11
Five gram sample																
<i>n</i>	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Mean	5311	28.3	0.67	7.98	222	526	16727	2140	227	12.3	627	2815	21.7	20.6	14.8	81.2
Median	5280	27.7	0.51	7.81	222	485	16885	2119	226	12.2	587	2776	21.2	20.6	14.9	78.6
Min	5090	27.0	0.485	7.66	216	434	15485	2060	221	11.9	579	2649	19.5	19.6	14.3	71.6
Max	5625	33.4	1.15	8.64	232	916	17285	2352	244	13.1	750	3079	25.9	21.9	15.1	122
STD	157.5	1.57	0.289	0.380	4.30	119	585.7	73.9	6.20	0.405	71.4	141	2.06	0.622	0.280	12.1
RSD (%)	3	6	43	5	2	23	4	3	3	3	11	5	9	3	2	15
Ten gram sample																
<i>n</i>	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Mean	5538	27.4	0.484	7.41	214	555	16492	2014	211	11.6	581	2622	16.7	22.0	14.5	75.3
Median	5484	27.9	0.485	7.42	215	538	16500	2035	213	11.6	581	2611	16.8	21.8	14.5	75.0
Min	5245	25.4	0.465	7.24	209	480	15455	1896	200	11.3	571	2554	15.5	20.6	13.9	66.1
Max	5900	28.7	0.495	7.57	218	686	17315	2104	218	11.8	598	2720	18.3	23.4	14.9	83.1
STD	224.1	1.18	0.010	0.118	3.16	62.7	466.1	74.6	6.18	0.149	7.81	54.2	0.791	0.990	0.341	5.01
RSD (%)	4	4	2	2	1	11	3	4	3	1	1	2	5	5	2	7
Change (%) ¹	8	-4	-50	-13	-2	19	6	-5	-8	3	-20	-8	-32	13	4	-5

¹Represents percent change between 0.5 and 10 g of material digested. *n* – number, Min – minimum, Max – maximum, ND – not detected, RSD – percent relative standard deviation, STD – standard deviation

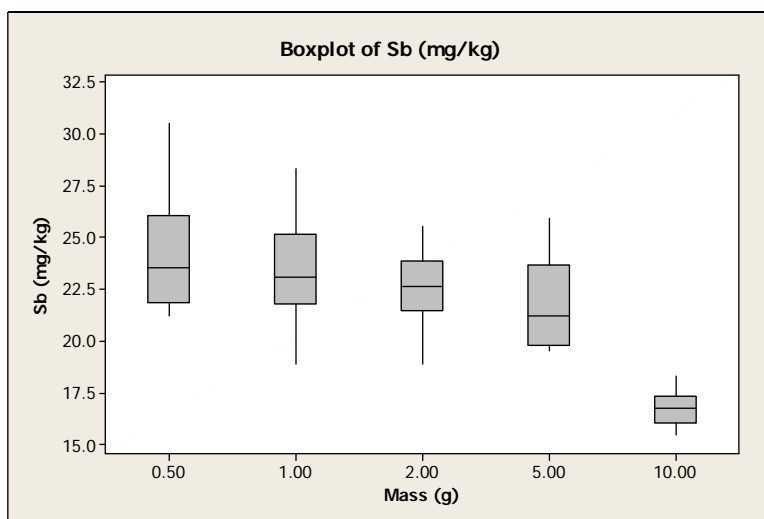


Figure 23. Box and whisker plots for antimony by digested soil mass.

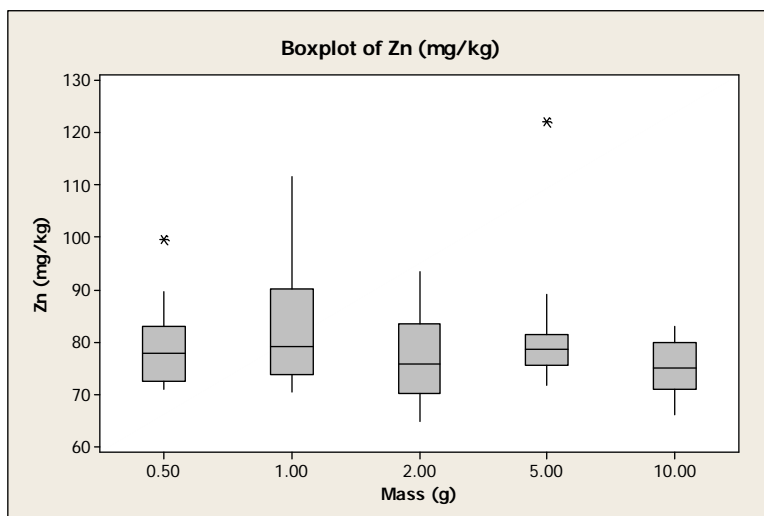


Figure 24. Box and whisker plots for zinc by digested soil mass.

However, Levene's test detected statistically significant differences in the variances at the 95% level of confidence for Pb and Sb. Increasing the digestion mass resulted in modest overall decreases in the variances for Pb and Sb. The non-parametric correlation coefficient Kendal's tau is equal to -0.80 for both the Pb and Sb scatter plots (Fig. 25 and 26) and indicates that the negative correlation between the digestion mass and standard deviation is significant at over the 90% level of confidence.

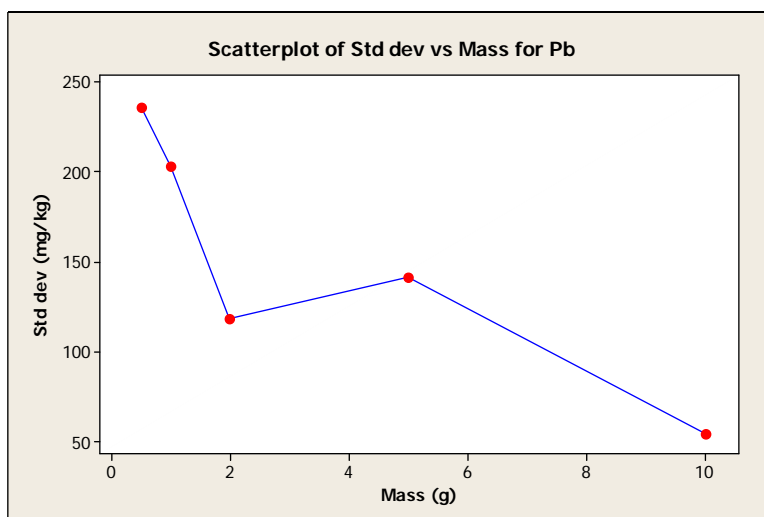


Figure 25. Scatter plot of the standard deviation for lead (mg/kg) versus the digestion mass.

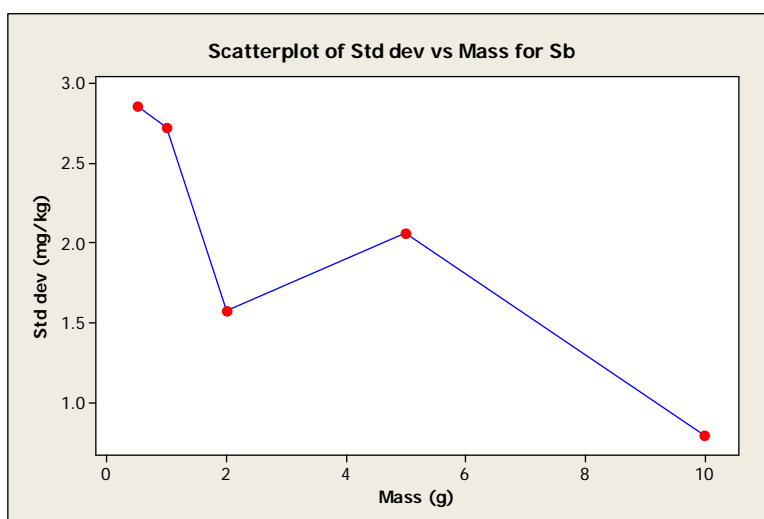


Figure 26. Scatter plot of the standard deviation for antimony (mg/kg) versus the digestion mass.

Increasing the digestion mass also seemed to introduce a small negative bias for both Pb and Sb. However, the mean and median concentrations of Pb and Sb appear to be negatively correlated with the digestion mass (Fig. 27 and 28). The KW test detected statistically significant difference in the medians for Pb and Sb at well over the 99% level of confidence.

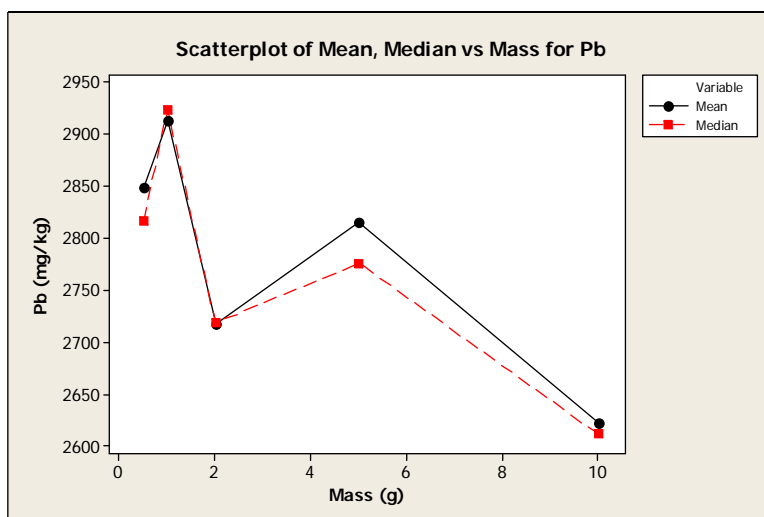


Figure 27. Scatter plots of the mean and median lead concentrations (mg/kg) versus the digestion mass.

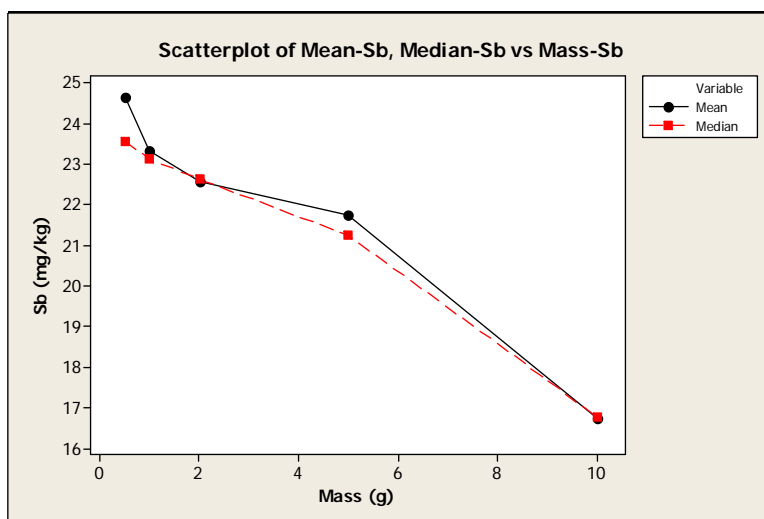


Figure 28. Scatter plots of the mean and median antimony concentrations (mg/kg) versus the digestion mass.

The scatter plots of the standard deviation versus the digestion mass for Cu and Zn (Fig. 29 and 30) do not show clear downward trends with increasing digestion mass. Levene's test did not detected statistically significant differences in the variances at the 95% level of confidence for these two metals.

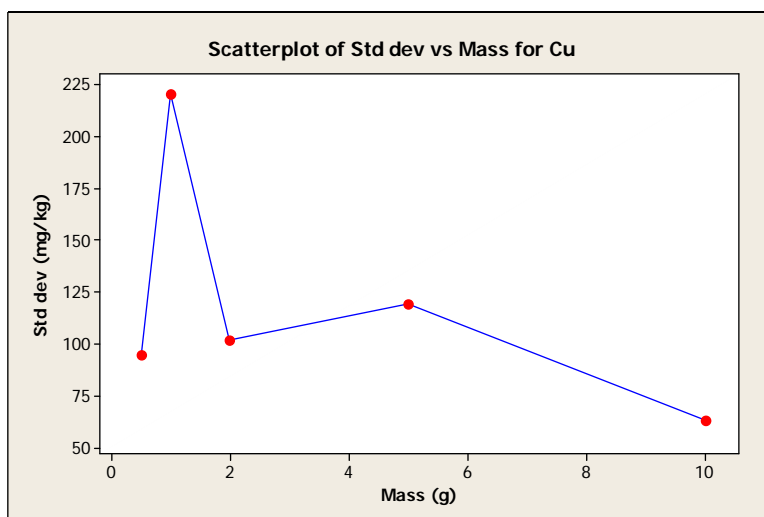


Figure 29. Scatter plot of the standard deviation for copper (mg/kg) versus the digestion mass.

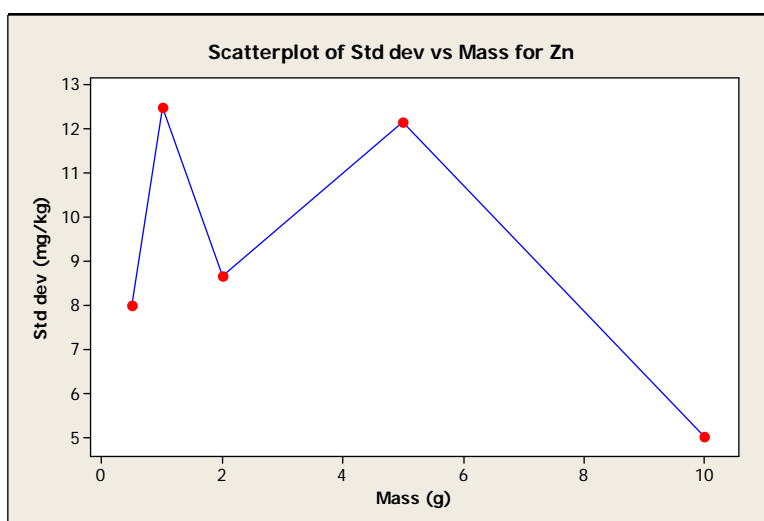


Figure 30. Scatter plot of the standard deviation for zinc (mg/kg) versus the digestion mass.

4.9 Digestion time

The effect of increasing the digestion time from 12 to 24 hr was assessed. The same 200-increment reference soil previously discussed was used for all tests. The same sample preparation, digestion, and analytical methods as discussed previously were used. The only parameter that was varied was the digestion time. All of the sample results for this set of experiments are included in Appendix A, Table A9.

A set of 30 replicates analyzed for the shorter digestion time and a set of 14 replicates was analyzed for the longer digestion time. Some descriptive

statistics for these two sets of results are presented in Table 29. The box and whisker plots for Cu and Pb (Fig. 31) and Sb and Zn (Fig. 32) suggest that increasing the digestion time does not strongly affect results. The median and IQR ranges for the two time intervals are similar for all four metals. Levene's test did not detect differences in the variances with 95% confidence for the two digestion times for any of the four metals. The KW test did not detect differences between the medians with 95% confidence for either Zn or Cu. However, the KW test did detect differences for the Pb and Sb medians with well over 99% confidence. These differences were relatively small; the medians for the two digestion times differ by less than 10%. Increasing the digestion time may have slightly increased the recovery of Pb and slightly decreased the recovery of Sb. The scatter plot (Fig. 33) shows that Pb and Sb are highly correlated, but the Sb concentrations decrease relative to the Pb concentrations when the digestion time is increased. Therefore, doubling the digestion time for 2-g masses, at best, only nominally affects method performance.

Table 29. Summary of metal results by different digestion time.

	Concentration (mg/kg)															
	Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	Zn
12-hour digestion interval																
<i>n</i>	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30	30
Mean	5816	30	2	9	223	550	16752	2125	225	12	611	2717	23	22	15	77
Median	5678	30	2	9	221	543	16920	2121	224	12	612	2718	23	22	15	76
Min	5425	26	2	8	214	391	14775	1905	205	12	571	2440	19	20	15	65
Max	6800	35	2	9	236	813	17715	2290	240	13	655	2936	26	26	16	94
STD	368.6	2.1	0.0	0.2	7.1	101.6	620.6	128.6	11.1	0.3	23.9	118.7	1.6	1.6	0.2	8.7
RSD (%)	6	7	2	2	3	18	4	6	5	2	4	4	7	7	1	11
24-hour digestion interval																
<i>n</i>	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Mean	5957	31.2	1.02	8.79	240	504	17065	2204	238	11.5	704	2865	20.6	23.3	16.0	80.2
Median	6075	32.1	1.05	8.94	242	498	17293	2259	243	11.7	630	2893	20.6	23.8	16.3	79.9
Min	5740	25.9	1.77	8.30	214	486	15530	1905	205	11.8	615	2440	20.3	21.9	14.7	64.7
Max	6215	33.7	1.09	9.06	248	726	17955	2303	248	11.9	910	3132	23.3	24.5	17.0	107
STD	438	2.51	0.068	0.477	11.0	116	984	165	16.8	0.77	163	231	1.34	1.80	0.95	12.4
RSD (%)	7	8	7	5	5	23	6	8	7	7	23	8	7	8	6	15
% Change ¹	8	-1	-44	0	5	2	2	-2	1	-8	19	4	-5	13	6	-1

¹Represents percent change between 24 and 48 hr. Min – minimum, Max – maximum, ND – not detected, RSD – percent relative standard deviation, STD – standard deviation, Highlighted text indicates known contaminants of interest present

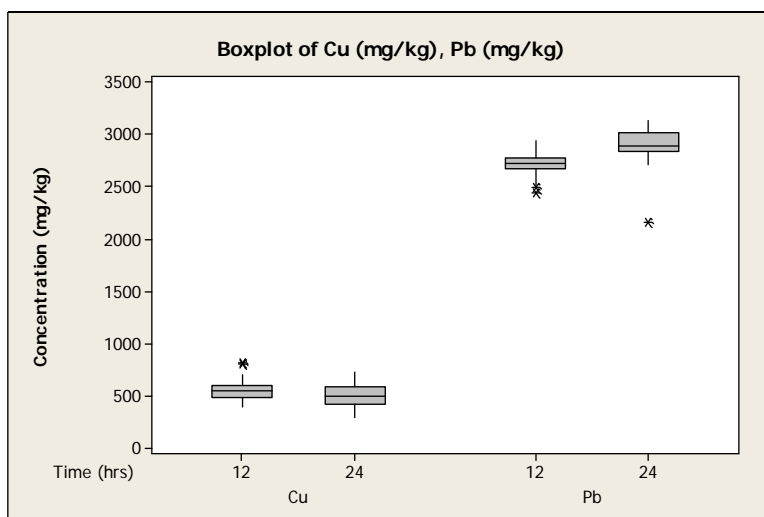


Figure 31. Box and whisker plots for copper and lead concentrations for two digestion times.

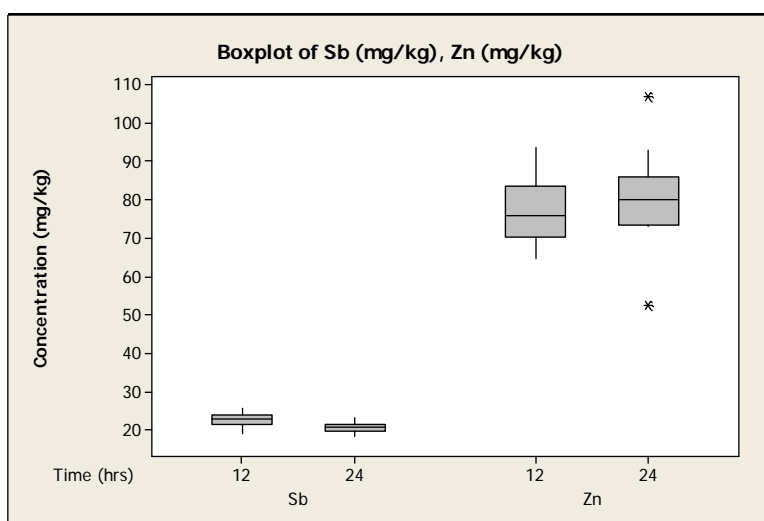


Figure 32. Box and whisker plots for antimony and zinc concentrations for two digestion times.

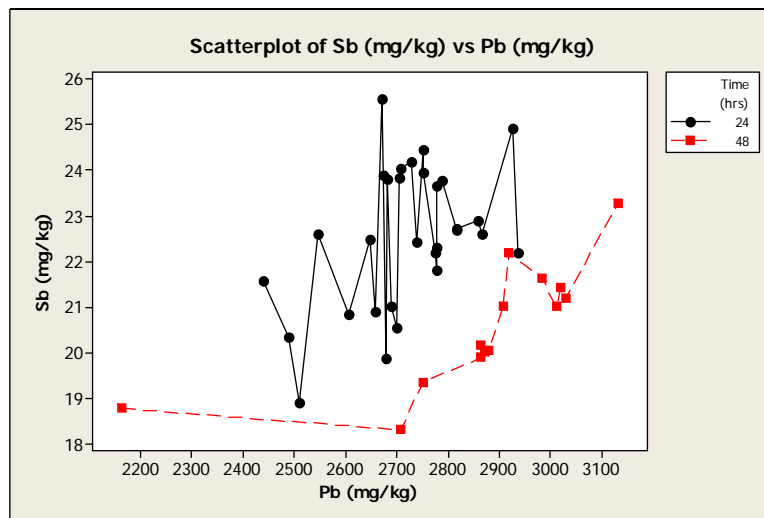


Figure 33. Scatter plots of antimony versus lead concentrations (mg/kg) for the two digestion times.

5 Discussion

The central question for this study is whether the current surface soil sampling and sample preparation procedures are appropriate for metal residues or whether modifications are necessary to the accepted standards. Soils are typically sampled by collecting discrete (grab) samples using either judgmental, simple random, or systematic-random sampling designs. Previous studies involving residue deposition of energetic compounds found that the accepted standard surface soil sampling and sample preparation techniques led to non-representative results and typically an under-prediction of the contaminant concentrations in the area of interest (Nieman 2007; Hewitt et al. 2005; Jenkins et al. 2004; Walsh et al. 2004). A preliminary study for metals, Table 5, shows the high degree of variability for grab samples from a military small arms range. Therefore, this study was conducted to compare the performance of the standard accepted surface soil sampling approach for the analysis of metals with multi-increment sampling.

The accepted standard soil preparation technique principally involves digestion of a subsample following USEPA Method 3050B. However, preliminary studies involving the collection of multi-increment surface soil samples from small arms ranges where metal residue deposition occurred indicated multi-increment field sampling was insufficient by itself to overcome the total sampling error (see Section 2.3). Therefore, changes to USEPA Method 3050B were evaluated including milling of the sample to reduce the particles to a uniform size.

5.1 Multi-increment soil sampling

The only direct means of determining the concentration representative of the entire DU would be to remove all of the soil and to digest/extract this material. In reality, it is impractical to perform this analysis, so the accuracy of the mean is generally unanswerable. One approach taken to attempt addressing the question of accuracy was to pool the entire MI sample data from the DU processed in similar manner. All of the MI sampling data from the same DU for samples with more than 30 increments and digestion masses of 2 g or more were pooled to estimate the “true” DU mean, resulting in a total of 22 field samples and 80 laboratory replicate analysis

(Table 30). Comparing the pooled MI sample results with the grab sample results indicates an under estimation of the DU grab sample mean relative to the MI samples.

A comparison of the mean and median values for the grab samples indicate a strong positive skew for the Cu, Pb and Sb data, whereas the mean and median values are very close to each other for the pooled data (Table 30). Large variability and positive skewed distributions is expected for discrete samples when soil contains a small number of metallic fragments containing these metals. The lack of a large positive skew for the Zn data suggests that the soil did not contain a significant number of metallic fragments composed of Zn.

Table 30. Mean concentrations of pooled grab samples and pooled MI samples for antimony, copper, lead, and zinc.

	Concentration (mg/kg)			
	Cu	Pb	Sb	Zn
Pooled MI sample size (<i>n</i>)	102	102	102	87
MI grand mean	546	2651	20.7	76.4
MI grand median	535	2679	20.9	75.6
Pooled grab sample size (<i>n</i>)	30	30	30	30
Grab grand mean	300	5060	87.8	66.1
Grab grand median	270	1238	10.0	61.9
Grab biased (<i>n</i>)	6	6	6	6
Grab biased mean	269	1161	10.9	59.4
Grab biased median	250	1103	8.79	59.4
MI-100 (<i>n</i>)	7	7	7	7
MI-100 mean	648	2929	22.8	81.8
MI-100	609	2638	20.7	78.2

MI – multi-increment sample

As the mean of the DU is unknown, the representativeness of a set of samples is primarily assessed in terms of the reproducibility of the results, which is measured by descriptive statistics such as the variance and relative standard deviation. As noted by Gerlach and Nocerino (2004), sampling can be the major source of error, particularly for soils containing heterogeneously distributed metal residues. The difference in soil concentrations from adjacent locations on a small arms range may be extreme. Table 31 presents the concentrations of lead for five co-located (within several centimeters) grab duplicates that were taken from a military small arms range in Alaska. The results indicate that there is large spatial heterogeneity possible. It is clear the fundamental error associated with compo-

sitional and distributional heterogeneity is not adequately addressed with analysis of a few number of grab samples. The error associated with the grab samples is sufficiently large that reliable estimates of the mean would be problematic.

To overcome the heterogeneity in soil samples from a small arms range, at least 30 grabs would likely be needed to obtain reliable estimates of mean metal concentrations. However, results of at least comparable quality can be achieved by collecting several replicate multi-increment samples consisting of at least 30 or more increments. Multi-increment field sampling resulted in lower RSDs than grab samples collected using a “grid-node approach” (i.e., systematic sampling) and often resulted in higher estimates of the mean. (Refer to Section 4.2 the discussion of for surface soil samples collected from the small arms range DU.) Replicate soil samples using the multi-increment sampling methodology resulted in RSDs of less than 30% (Section 4.2), suggesting that distributional heterogeneity was reasonably controlled.

Table 31. Lead concentrations of five sets of duplicate surface soil samples from small arms range in Alaska; each pair was collocated within several centimeters.

Sample number	Lead (mg/kg) field replicate 1	Lead (mg/kg) field replicate 2	%RSD
1	68	72	6
2	246	446	58
3	73	347	130
4	978	528	60
5	1010	79	171

Gy's theory indicates that to obtain a representative sample it is necessary to reduce the fundamental error of a sample by increasing the sample mass and number of increments collected per sample. Although the number of increments necessary per sample will be site dependent, the data from this study indicate the variance decreases for all metal analytes once 30 or more increments are collected (Fig. 34 and 35). The lack of a consistent trend is owing to the small number of replicate samples collected. Only a set of seven replicate multi-increment soil samples was collected for each per increment population. If a larger number of replicate samples, > 30, had been collected for each increment population, a clearer trend of increased precision with increasing number of increments is expected.

The box and whisker plots for Cu, Pb, Sb, and Zn show overall decreases in the IQRs and range of values (Fig. 36–39). The reduction in variability with increasing number of increments per sample is similar to the observations for MI soil samples containing energetic residues (Jenkins et al. 2006a, 2005, 2004a,b; Hewitt et al. 2005a; Walsh et al. 2005). Although the findings from this study are only representative for the site evaluated, the similarity of findings with the energetic work (Hewitt et al. 2009) strongly suggests 30 or more increments are warranted for soils (Gerlach and Nocerino 2004) expected to contain metallic residues. Because the fundamental error can only be estimated prior to sampling, Gy's formula highly recommends that 50 to 100 increments be collected when evaluating soils from military small arms ranges.

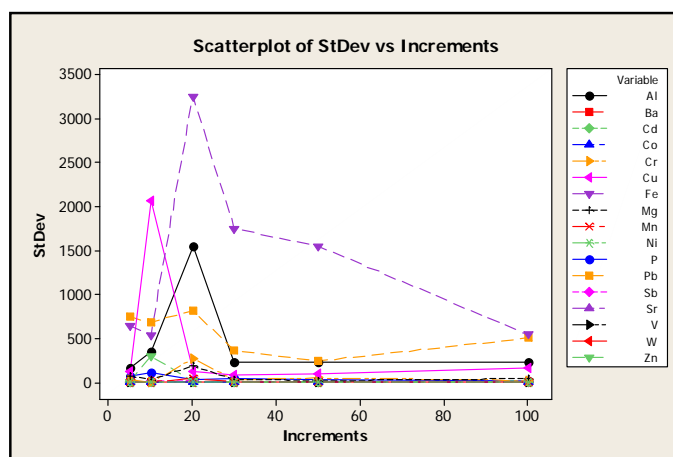


Figure 34. Standard deviations (mg/kg) of various metals vs. numbers of increments per multi-increment sample.

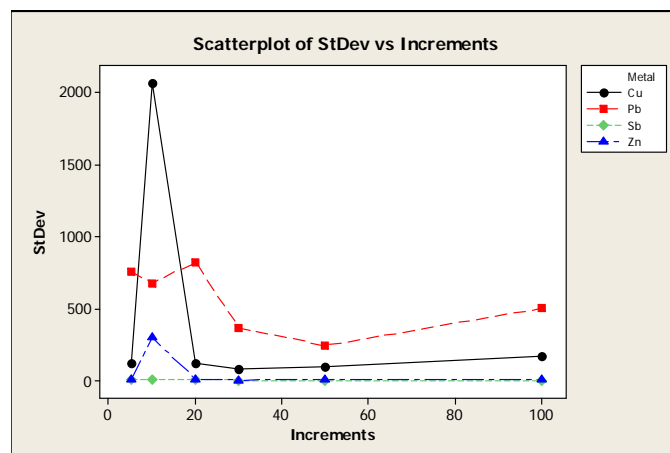


Figure 35. Standard deviations (mg/kg) of copper, lead, antimony and zinc vs. number of increments per multi-increment sample.

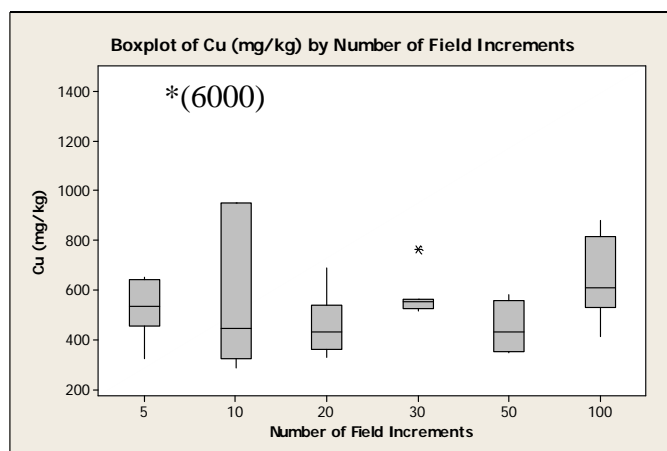


Figure 36. Whisker and box plots of copper results by number of field increments.

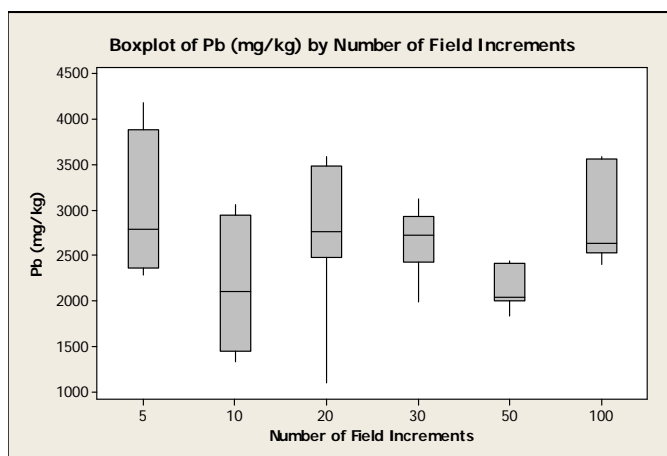


Figure 37. Whisker and box plots of lead results by number of field increments.

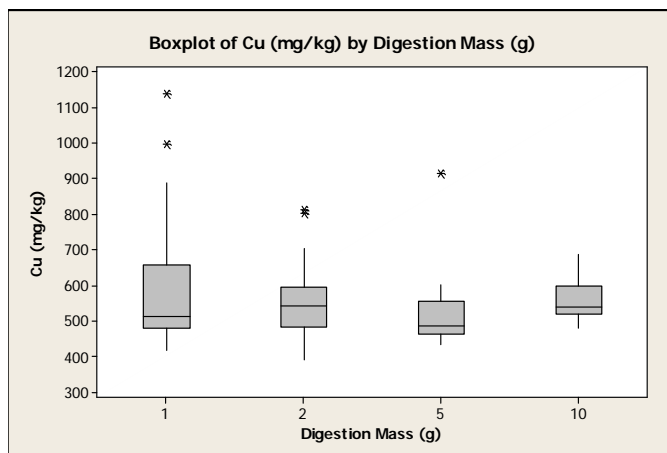


Figure 38. Box and whisker plots of antimony results by number of field increments.

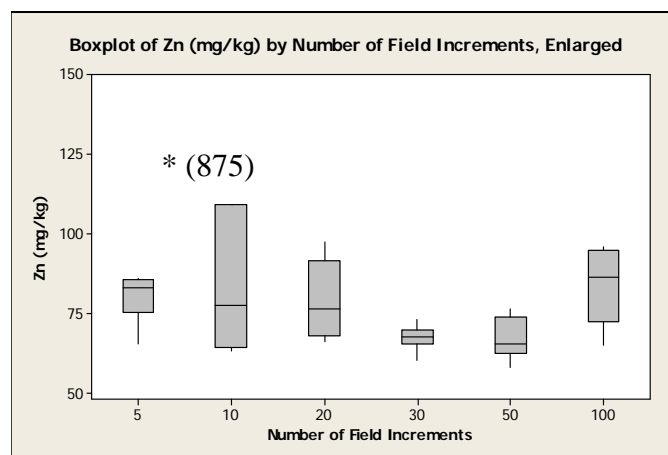


Figure 39. Box and whisker plots of zinc results by number of field increments.

Table 32. Determination of number of sample increments needed to achieve a desired soil sample mass with CMIST corer knowing the diameter of the corer, a sampling depth of 2.5 cm and a soil density of 1.5 g/cm³ (Walsh 2009).

Corer Diameter (cm)	Sample Mass* (g)				
	500	750	1000	1500	,000
	Number of increments to reach sample mass (g)				
1.00	170	255	340	509	679
1.25	109	163	217	326	435
1.50	75	113	151	226	302
1.75	55	83	111	166	222
2.00	42	64	85	127	170
2.25	34	50	67	101	134
2.50	27	41	54	81	109
2.75	22	34	45	67	90
3.00	19	28	38	57	75
3.25	16	24	32	48	64
3.50	14	21	28	42	55
3.75	12	18	24	36	48
4.00	11	16	21	32	42
4.25	9	14	19	28	38
4.50	8	13	17	25	34
4.75	8	11	15	23	30
5.00	7	10	14	20	27
* Assumed: Dry bulk soil density = 1.50 g/cm ³ , increment core length = 2.5 cm					

Having addressed the number of increments needed per sample the question is how much sample mass is needed to reduce the fundamental error

to acceptable levels. Although this specific issue was not addressed in this study, previous work with energetics suggests a minimum of 1 kg of material is appropriate minimum (Hewitt et al. 2009). Table 32 provides a means to estimate the number of increments needed with a given CMIST corer diameter to achieve a given mass of soil. For example, using a 2.0 cm corer to a depth of 2.5 cm requires 85 increments to achieve a sample mass of 1 kg.

5.2 Field splitting

Many commercial environmental laboratories are not equipped to handle the large sample volumes that result from multi-increment sampling. Unfortunately, owing to heterogeneity, the volume of a sample shipped to a laboratory for processing and analysis cannot readily be reduced in the field in a manner that does not compromise the quality of the original sample. As shown in Section 4.4, field splitting using the cone-and-quartering techniques (prior to laboratory sample preparation) gives variable results for the four splits, especially when soil contain metal fragments.

Although rotary splitters tend to produce results that are more representative than other splitting techniques such as cone and quarter (Petersen et al. 2004; Gerlach and Nocerino 2003), even rotary splitters may not adequately control sample heterogeneity when soils contain metallic fragments. Table 7 presents results for two samples obtained from a military small arms range where the samples were split with a rotary splitter prior to milling and digestion following USEPA Method 3050B. The rotary splitter addresses the distributional heterogeneity within the sample by collecting very large number of increments. In this example, a 25-kg sample was used so the splits had adequate mass for the individual samples. Sample 1, split 1 has a copper concentration of 2600 mg/kg whereas split 3 of the same sample has a concentration of 110 mg/kg. Without analyzing each sample split multiple times, it may not be obvious which value is more representative of site conditions. Therefore, simple field splitting techniques such cone-and-quartering will likely be ineffective for controlling heterogeneity relative to laboratory sampling processing techniques (e.g., milling). Petersen et al. (2004) states:

...all grab sampling and shoveling methods must be totally avoided: indeed grab sampling should never be used in practice—with the singular exception for thoroughly homogenized fine powders.

5.3 Milling

To evaluate whether milling was appropriate for soil samples from small arms ranges a comparison was made between an unground sample and a sample milled with a puck mill (Section 4.5). The results for Cu, Pb, Sb, and Zn were evaluated in depth, as these metals are typically the major constituents of small arms ammunition. Milling normalized the distributions and increased median metal concentrations. Figures 40 and 41 are probability distributions for lead for the unground and ground replicate samples, respectively. Note that the p-value for the normality test for the set of unground replicates ($n = 15$) is < 0.001 , indicating the null hypothesis that the distribution is a normal distribution can be rejected with over 99.9% confidence. The p-value for the set of ground replicates ($n = 30$) is > 0.1 (i.e., the normality assumption cannot be rejected with at least 90% confidence).

Milling nearly doubled the estimated mean concentration of Pb and Sb. The mean Cu concentration increased by 50% and the mean concentration of Zn by 20% (Fig. 42 and 43). However, milling decreased the variability of Pb and Sb significantly (Fig. 44 and 45). Statistically significant differences in the variances of the mean were not observed for Cu and Zn at the 95% level of confidence.

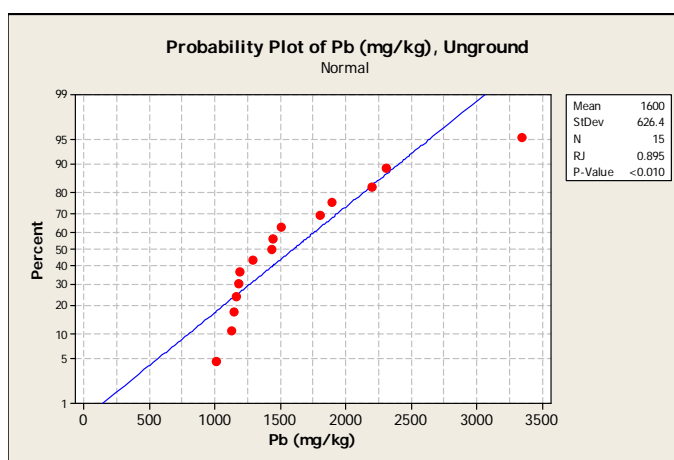


Figure 40. Normal probability plot for unground lead (replicates).

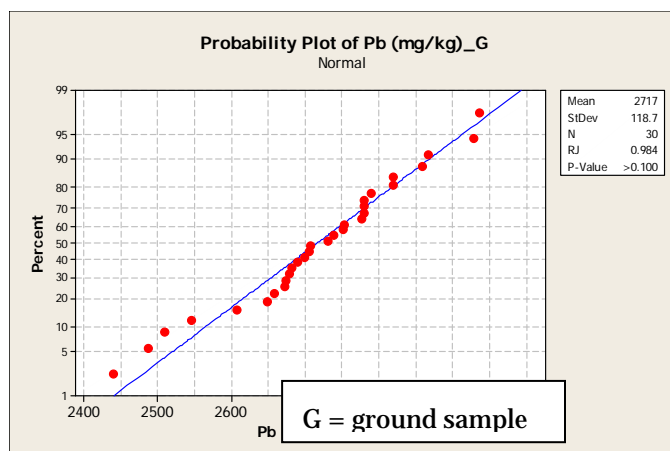


Figure 41. Normal probability plot for ground lead replicates.

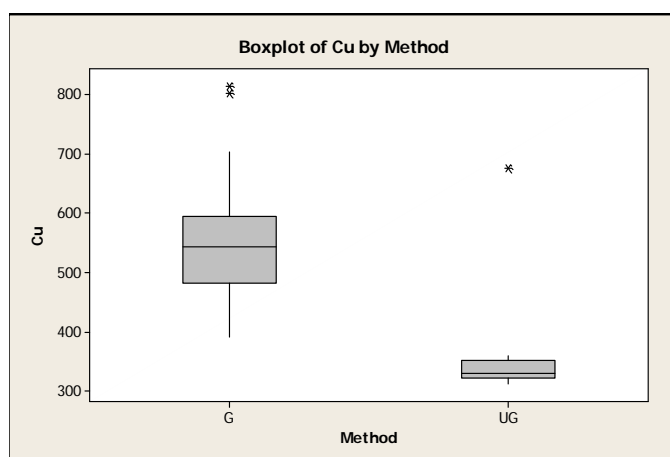


Figure 42. Box and whisker plots for ground (G) and unground (UG) copper (mg/kg) replicates.

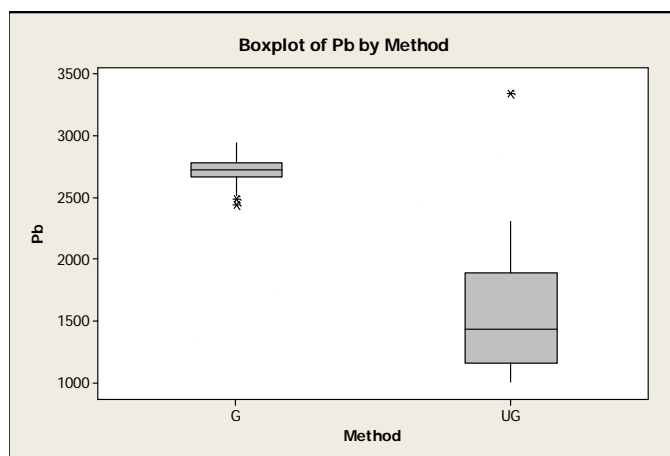


Figure 43. Box and whisker plots for ground (G) and unground (UG) lead (mg/kg) replicates.

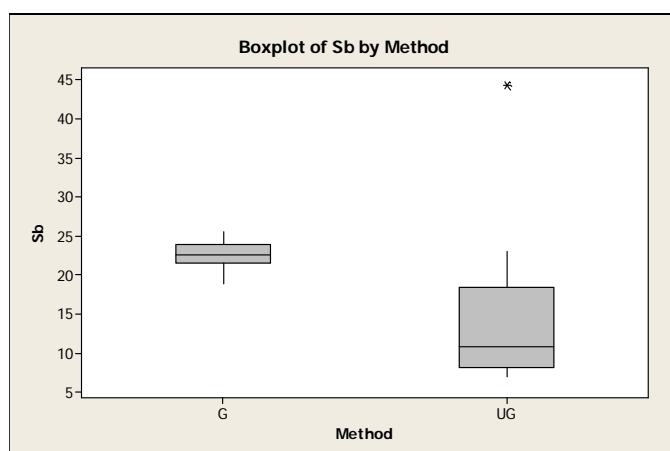


Figure 44. Box and whisker plots for ground (G) and unground (UG) antimony (mg/kg) replicates.

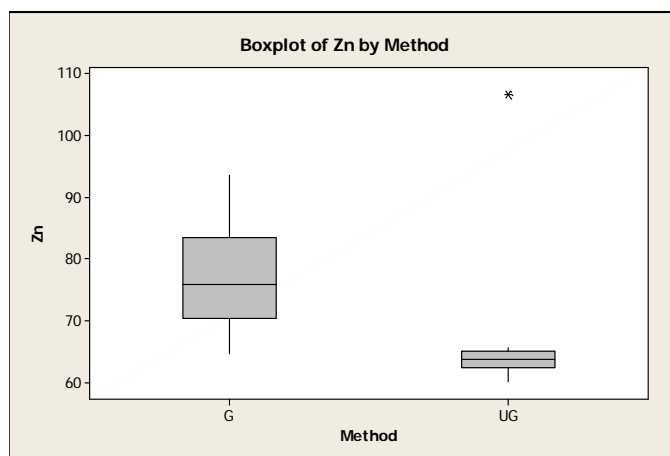


Figure 45. Box and whisker plots for ground (G) and unground (UG) antimony (mg/kg) results.

Because the samples were milled using the puck mill (which contains metal components) and ball mill, one question is how much does cross-contamination from the milling equipment contribute to the increased metal values. The metal content of the puck and bowl used is known and a calculation was used to assess the metal contribution to the sample (Table 33). The approach attempts to estimate the increase in metal concentration owing to the puck's mill grinding surfaces. As a "worst-case" scenario, it was assumed that 1 mg of the bowl and puck abraded and released into soil sample during grinding. Lab Tech Essa provides information on the approximate metal composition of the bowls and puck it sells. The device used at CRREL consisted of bowls and puck made of chrome steel. Assuming a soil concentration of 1 mg/kg a calculation was made on the amount of metal increase coming from the bowl. Table 32 indicates that the potential exists for a significant increase in Cr, Mn, Ni, and V concentrations as

a result of cross-contamination from a metallic puck and bowl. However, the potential impact on the metals of interest Sb, Cu, Pb, and Zn is minimal. Further the cross-contamination issue becomes less important as the metal concentration of the sample increases. For Sb, Cu, Pb, and Zn the potential concentration increase from cross-contamination is < 5 mg/kg. Small arms range soils often have Pb levels, typically the principal metal of interest, in the 100 to 100,000 mg/kg range.

One thought to assess the contribution of metal to the sample from milling is through careful recording of the soil weight pre- and post-milling. However, these measurements typically indicate a metal loss from pre to post milling instead of a gain. This is primarily due to the inability to contain the entire sample upon opening the bowl and transferring it to the sample container. Some of the particle sizes are very small and become airborne during the transfer step resulting in a sample loss. Given the contribution from the puck and bowl is likely very small the mass contributed is immeasurable.

Another comparison was made between unground and ground glass as discussed in Section 4.1, which indicate that metals such as Al, Cr, and Fe are contributed to the sample as part of the grinding process. However, as shown in Table 9 the cross-contamination of the sample is minimal for Cu, Pb, Sb, and Zn.

A mortar and pestle, which only disaggregates a sample, reduced laboratory sub-sampling variability compared relative to processing without any milling, but the %RSDs of laboratory replicates, did not generally meet the 15% performance criterion. The %RSDs for Sb, Cu, Pb and Zn are 55, 39, 32, and 28%, respectively (Table 18). It is possible that the variability can be reduced by additional grinding with the mortar and pestle. However, as manual grinding using a mortar and pestles is very labor-intensive, this approach will likely be impractical for processing large numbers of samples (e.g., given that grinding a large number of MI soils samples can rather labor-intensive even when done using a puck mill). Therefore, the mortar and pestle is not recommended when for milling soil samples that are expected to contain metallic particles.

Table 33. Estimate of metal contribution from puck mill to sample

	Al	Ba	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	W	Zn
Mean unground (mg/kg)	4124	17	1	6	6	357	9307	2018	201	9	559	1600	14	13	10	ND	66
Ground (mg/kg)	5509	32	2	9	229	496	16676	2242	235	12	590	2760	22	21	15	ND	81
Concentration increase unground to ground (mg/kg)	1384	14	1	2	223	139	7369	225	34	3	31	1160	8	8	5	ND	15
% change unground to ground	34	85	69	35	3641	39	79	11	17	37	5	73	53	64	52	NA	23
Max bowl metal concentration (mg/kg)	U	NA	NA	NA	1×10 ⁵	1990	5×10 ⁵	NA	3700	3030	NA	7	18.4	NA	1140	1210	52
Calculated soil concentration (mg/kg) ¹	NA	NA	NA	NA	225	5	999	NA	8	7	NA	1	1	NA	3	3	1
Mean% Metal Contribution from puck mill	NA	NA	NA	NA	99	4	14	NA	24	47	NA	<1	14	NA	63	ND	7

¹Assumes 1 mg of material of erosion from bowl and puck and 500 mg of soil milled with the metal concentration of the soil being 1 mg/kg.

NA – not applicable, ND – not determined, U - unknown

Blue highlighted text indicates known metal constituents present in the bowl and puck of the puck mill

Yellow highlighted text indicates known contaminants of interest present and constituents present in the bowl and puck of the puck mill

Therefore, milling of a soil samples containing small arms range metals in particulate form is appropriate with either the ball mill or puck mill. Note, however, that a ball mill is not appropriate for milling soil samples that contain propellant fibers. Therefore, soil samples collected from a small arms range firing point that may contain metallic and propellant residues would require use of the puck mill.

A prior unpublished study investigated the performance of a ceramic disc grinder for milling but the device produced poor results, and was virtually impossible to thorough decontaminate to avoid significant sample cross-contamination. Research using a pulvisette for milling is ongoing. Preliminary results with an unsieved soil (unpublished), yielded poor reproducibility but this may have been a function of the large metal residues present in the sample. Additional work using sieved soil is planned.

The necessity of milling depends on a number of factors that need to be evaluated on a project-by-project basis, which typically include the expected soil concentrations of the metals of interest, how close these values are to the regulatory thresholds or cleanup levels and the decisions the data will support. The expected metal concentration, principally lead, for soil from the berm face of a military small arms range may be well above the USEPA Preliminary Remediation Goal (PRG) of 400 mg/kg. Milling may not be necessary to determine whether the mean Pb concentration exceeds this value. The large variability of the unground soil may not affect decisions (Clausen et al. 2010). However, milling may be necessary if sampling is being done after cleanup to verify residual contamination is less than the cleanup goal. Similarly, the sampling of the range floor and firing points is likely to result in a lower lead concentration. Better precision is typically needed as the mean contaminant concentrations approach the project's decision limits.

5.4 Sample digestion

The digestion mass of the sample and the digestion interval were two variables assessed during the sample preparation process following USEPA Method 3050B. It was expected that increasing the digestion mass would decrease the sample error. Overall decreases for the variance were observed for Sb and Pb as the digestion mass was increased. Based on a visual examination of the whisker and scatter plots (the standard deviation versus the digestion mass) in Section 4.8, laboratory sub-sampling precision improves overall as the digestion mass increases but the changes

seem nominal when the digestion masses ≥ 2 g. The sample sizes may have been too small to consistently detect statistical differences in variances, especially for the larger digestion masses. The scatter plots of the standard deviation for Pb and Sb versus the digestion mass are similar in appearance and all exhibit downward trends. However, the variability was too large for Zn and Cu to observe a clear downward trend.

Our recommendation is to digest a minimum of 2-g of material and where practical to digest a larger mass, especially precision is important consideration. However, it is noted that digestion masses ≥ 10 g are not viable possible using standard-size digestion blocks and require digestions using larger sample vessels on hotplates. It is also cautioned that even 2–5 g digestion masses may cause problems for digester blocks because of analyte losses owing to foaming after acid additions

Table 34. Results of the KW test for differences between median of the 12 and 24 hr digestion times for various metals.

Metal	KW p-value	M ₁₂ (mg/kg)	M ₂₄ (mg/kg)
Al	0.082	5678	6075
Ba	0.036	30.29	32.09
Cd	0.000	1.825	1.050
Co	0.000	8.60	8.935
Cr	0.000	221.2	242.1
Cu	0.236	542.5	498.2
Fe	0.014	16920	17293
Mg	0.015	2121	2259
Mn	0.000	223.9	242.8
Ni	0.000	12.24	11.67
P	0.049	612.3	630.0
Pb	0.000	2718	2893
Sb	0.000	22.61	20.59
Sr	0.002	21.51	23.80
V	0.000	15.14	16.32
Zn	0.241	75.80	79.88

M₁₂ = Median of results for 12-hr digestion

M₂₄ = Median of results for 24-hr digestion

KW = Kruskal-Wallis Test

Largest median bolded if p-value < 0.05 (i.e., medians significantly differ at 95% level of confidence).

The length of the digestion interval had a slight affect on the measured metal concentrations. The median concentrations tended to increase when

the digestion time was doubled. Statistically significant differences at the 95% level of confidence were reported from the KW test for 13 of the 16 metals (Table 34). For the four small arms metals Cu, Pb, Sb and Zn, statistically significant differences were observed for Sb and Pb only. Increasing the digestion time increased the Pb median and decreased the Sb median. The lower Sb concentrations are presumably owing to volatilization losses, an occurrence that is well documented (Nash et al. 2001; Hewitt and Cragin 1991; Kimbrough, 1989). However, the amount of concentration increase was small, generally less than 10%. Therefore, the recommendation is that no changes be made to the digestion time for USEPA Method 3050B.

5.5 Antimony

The concentrations of both Pb and Sb seem to decrease with increasing sample mass (Section 4.8). The mechanism responsible for this decline is unknown. However, USEPA Method 3050B often yields poor Sb recoveries, typically < 50% (Nash et al. 2001; Hewitt and Cragin 1991; Kimbrough, 1989). This is primarily because some of the Sb is insoluble as a result of passivation and chemical bonding with the soil particles.

The following digestion option (described in a footnote for Sb in USEPA Method 3005) was investigated:

- Weigh out 1.0 to 1.2 g of the soil sample into the digestion vessel using sub-sampling.
- Add 2.5-mL concentrated HNO₃ and 2.5 mL concentrated HCl to the sample.
- Cover with a watch glass and reflux on hot block set at 95°C (covered container of water) for 15 minutes.
- Filter through Ahlstrom 55 into 100-mL vessel while still hot.
- Rinse with hot 1.25mL (~95°C) concentrated HCl.
- Rinse 3× with hot (95°C) reagent water (5 mL rinses).
- Place the filter paper and soil residue back into the original sample digestion vessel. Then add 2.5 mL concentrated HCl, cover and reflux on hot block for 20 minutes or until paper dissolves.
- Filter digestion solution through Ahlstrom 55 adding to the original filtrate. Rinse 3 times with reagent grade water. (5 mL rinses.).
- Bring to final volume of 100 mL with reagent grade water.

This is also the routine procedure that produces acceptable results in the USDOE MAPEP proficiency-testing program. Preliminary testing of this method on the unground (control) sample yielded improved Pb and Sb recoveries and significantly reduces the total sampling error as calculated with the percent RSD (Table 35). The difference in mean values was evaluated with a t-test at $p = 0.05$ for $n = 15$ and the results indicate the difference in Pb levels is not statistically significant. However, the differences in mean values for Sb are statistically significant.

Table 35. Antimony and lead recoveries with USEPA Method 3050B and a modification to USEPA Method 3005 for an unground soil.

	Mean (mg/kg)			
	Lead Method 3050B	Lead Method 3005 modified	Antimony Method 3050B	Antimony Method 3005 modified
<i>n</i>	15	15	15	15
Mean	2043	2110	16	45
Median	1600	2000	10	38
Min	1030	1330	4	25
Max	5190	3370	61	92
STD	1251	605	18	19
RSD (%)	61	29	116	42

Min – minimum, Max. – maximum

STD – standard deviation

RSD - percent relative standard deviation

A similar analysis was done for an unsieved sample ground with the puck mill and ball mill (Table 36). In this case, there was no difference between the mean Sb and Pb concentrations with the two methods based on a t-test analysis. However, the calculated RSDs were lower with the Modified Method 3005 procedure resulting in a more precise estimate of the mean. Therefore, if Sb is a contaminant of concern and the measured soil concentration is expected near the regulatory threshold the modified USEPA Method 3005 should be considered.

Table 36. Antimony and lead recoveries with USEPA Method 3050B and a modification to USEPA Method 3005 for soils ground with puck and ball mills.

	Mean (mg/kg)			
	Lead Method 3050B	Lead Method 3005 modified	Antimony Method 3050B	Antimony Method 3005 modified
Puck and ring	22336	22320	186	185
Ball mill - 8 hr	4798	4787	35.0	34.9
Ball mill - 12 hr	5810	5800	46.1	45.9
Ball mill - 16 hr	6375	6380	44.9	45.1
Ball mill - 20 hr	7153	7153	55.2	55.2
	Relative standard deviation (%)			
Puck and ring	37	5	39	9
Ball mill - 8 hr	13	10	23	20
Ball mill - 12 hr	6	4	7	7
Ball mill - 16 hr	6	1	14	7
Ball mill - 20 hr	1	1	1	2

Another option explored by the Swiss involves the addition of citric acid to the nitric acid allowing Sb to form stable complexes and oxyacids that are soluble.

6 Conclusion

Field studies of active small arms ranges where metal residues are deposited indicate that metals concentrations in soils exhibit large spatial heterogeneity. Traditional grab sampling and laboratory preparation procedures for soils containing metal residues are not sufficient to give representative or reproducible results for the characterization of anthropogenic metal contamination.

The multi-increment sampling approach provides reproducible for soils containing metal residues from the firing of small arms weapon systems. Distributional heterogeneity is addressed by collected at least 30–100 increments over the entire DU using systematic or simple random sampling. Owing to the large number of increments collected within a DU, multi-increment sampling tends to result in better spatial coverage and larger (and therefore more representative) sample masses for laboratory analysis than conventional grab sampling designs, which typically entail a comparative small number of grabs (e.g., $n = 10\text{--}20$). However, multi-increment field sampling is insufficient in of itself to overcome the distributional and compositional heterogeneity in the soil samples. Modifications to laboratory sample preparation procedures are also necessary to reduce variability owing to sample heterogeneity.

One of the issues to arise with the multi-increment soil sampling is the large volume of soils collected and then shipped to the analytical laboratory. Field processing using a splitting technique such as cone-and-quartering to reduce soil volume yields non-representative results, i.e., the concentration of metal in the different quarters is not the same. Although, collecting many increments randomly of a DU reduces the total variability, this alone is not sufficient in of itself to overcome heterogeneity. Therefore, field splitting to reduce sample volume is not an acceptable approach. Other processing steps that are best done in controlled environment of an environmental laboratory are necessary before sample splitting can occur. If metal residues are present in the sample it is necessary to mill the sample to reduce the size of the metal fragments present in the soil to a common particle size. Without milling, there will usually be large variability, resulting in unreliable estimates of anthropogenic metal concentrations. Two types of milling equipment yielded satisfactory results 1) ball mill and

2) puck mill. Milling for 5×60 s with a puck mill is sufficient to reduce the total sampling error to <30% for field replicates and < 15% for laboratory replicates. Similar levels of total sampling error were associated with milling using the ball mill for 18 hr.

One issue to be aware of when using a puck mill, which contains metallic components, is cross-contamination of the soil sample. The principal metals identified coming off the puck mill are Al, Cr, and Fe. However, metal cross-contamination is not a particular concern for the small arms range metals (Sb, Cu, Pb, and Zn). If metal residues composed of Al, Cr, and Fe are expected then use of the ball mill would be preferred or the puck mill with an agate bowl and puck. Use of the puck mill with metallic components would require studies using control materials to quantify the amount of metal contribution from the bowl and puck to the soil sample.

Other sample processing changes during the digestion step evaluated such as digestion mass and digestion interval had little bearing on the measured metal values. However, it was noted that Sb recoveries were poor with guidance provided in USEPA Method 3050B and therefore an alternative method was recommended to improve sample recoveries.

7 Recommendations

For small arms ranges it is desirable to treat the firing point and berm face as separate DUs. In most cases, it is not necessary to sample the range floor located between the firing point and berm face because most projectiles do not land in this area. Previous studies have verified that little metal is contributed to the range floor.

To reduce the influence of distributional heterogeneity in the estimate of the mean concentration for a decision unit, it is recommended that at least 50 evenly spaced increments are collected to form a multi-increment sample that weighs between 1 and 2 kg. The objective of collecting multi-increment samples using a random systematic design is to obtain a proportional amount of contamination particles of every composition and shape to what exists within the selected decision unit and not to over or under sample any portion of the decision unit. The depth interval of the sample should be several inches or centimeters. Our recommendation is to collect a minimum of 3 replicate samples from the DU.

Once the MI sample has been collected it needs to be processed. This involves air-drying, sieving, machine grinding, and sub-sampling the multi-increment sample before a portion of it is digested and analyzed. The entire field-moist multi-increment sample is spread onto an aluminum-foil-lined tray and air-dried at room temperature ($<25^{\circ}\text{C}$). The time required to thoroughly air-dry a sample depends on the relative humidity and the initial soil moisture content. Generally, 2 to 3 days are required.

For unvegetated or sparsely vegetated soil samples work the air-dried sample through a no. 10 sieve. The no. 10 sieve has a mesh with 2-mm openings, the size division between coarse sand and gravel (USDA 1993). A stainless steel spoon is used to break soil aggregates and dried vegetation such as moss or grass while sieving. Each size fraction is weighed, the $< 2\text{-mm}$ fraction is processed further as described below, and the oversize ($>2\text{-mm}$) fraction is saved in the original sample bag for further study if desired. Sieving should be done in an exhaust hood to control dust.

The preferred method of milling soil samples for energetics and metals uses a ring-mill (also called a puck mill) grinder that works for crystalline

explosives, propellants, and metals. A ball mill may be appropriate when the focus is solely on metals. Under the metals only scenario, 18 hr of milling appears to be sufficient for most soil samples from a military small arms range when metal residues are expected. The ball mill is not appropriate for firing point samples when energetics and metals are planned to be analyzed. Soils from ranges that contain propellant residues (i.e., firing points, disposal areas, rocket impact ranges) should be ground in a puck mill for five 60-s periods with a 5 minute cooling time between each grind. The extra grinding time is needed to pulverize the propellant fibers, because these are mainly composed of nitrocellulose, a wood-like substance, and the cooling times are to avoid overheating and volatilizing the energetics. For metals the 5 minute grind times used for propellant have also been found to be effective. Grinding reduces the particle size of the coarse soil to the texture of flour ($<75\ \mu\text{m}$). The ground multi-increment sample should appear and feel uniform when portions of the ground soil are pinched and rolled between the thumb and index finger. There should be no un-ground grains or fibers. If needed, the soil should be ground for an additional 60 to 90 seconds. If the puck mill is used with metallic components and Al, Cr, and Fe are contaminants of concern then studies should be conducted to quantify the cross-contamination.

During weighing out the 2 to 10 g of milled $< 2\text{mm}$ soil for digestion a subsampling approach involving a minimum of 20 increments is recommended. For the most part collecting a multi-increment field sample and milling of the soil will reduce the total sampling error to acceptable levels for most metals. However, in some cases, metal residues, such as Cu, may remain in the soil thus resulting in a less precise estimate of the mean. Sub-sampling during digestion preparation will result in a more representative sample.

Finally, it is recommended that all of the previous discussion be incorporated into a revision of USEPA Method 3050B including an Appendix to discuss multi-increment field sampling. Inclusion of an Appendix to discuss the multi-increment sampling methodology was the approach utilized when modifying the energetics extraction procedure, USEPA Method 8330B.

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Appendix A: Analytical Results

Table A1. Experiment 1—Glass bead metal results.

Experiment ID	Lab Replicate	Unground	Grinder Type	Ground Time (sec)	Al (mg/kg)		Ba (mg/kg)		Ca (mg/kg)		Cd (mg/kg)		Co (mg/kg)		Cr (mg/kg)		Cu (mg/kg)	
B38-6	1	x	NA	NA	2.45	J	0.140	U	NA		-0.125	U	-0.005	U	0.030	U	1.25	J
B38-7	2	x	NA	NA	3.22	J	0.165	U	NA		-0.185	U	-0.035	U	0.010	U	1.16	J
B38-8	3	x	NA	NA	6.48	J	0.160	U	NA		-0.190	U	-0.055	U	0.005	U	1.23	J
B38-9	1	NA	Puck	1x60	142		0.655		NA		-0.125	U	0.200		89.5		1.91	
B38-10	2	NA	Puck	1x60	134		0.650		NA		-0.125	U	0.200		90.6		1.89	
B38-11	3	NA	Puck	1x60	150		0.660		NA		-0.115	U	0.190		90.6		1.98	
B38-12	1	x	NA	NA	2.22	J	0.100	U	NA		-0.205	U	-0.045	U	-0.015	U	1.22	J
B38-13	2	x	NA	NA	1.87	J	0.100	U	NA		-0.205	U	-0.040	U	-0.005	U	1.19	J
B38-14	3	x	NA	NA	1.93	J	0.085	U	NA		-0.200	U	-0.050	U	-0.025	U	1.15	J
B38-15	1	NA	Puck	1x60	37.5		0.205	U	NA		-0.190	U	0.000	U	10.3		1.41	J
B38-16	2	NA	Puck	1x60	34.1		0.190	U	NA		-0.195	U	0.000	U	10.4		1.40	J
B38-17	3	NA	Puck	1x60	30.4		0.200	U	NA		-0.195	U	0.000	U	9.91		1.43	J
B45-6	1	NA	Puck	1x60	128		0.685	J	NA		0.057	J	0.118	J	58.2		1.93	
B45-7	2	NA	Puck	1x60	142		0.680	J	NA		0.045	J	0.125	J	57.0		1.83	
B45-8	3	NA	Puck	1x60	144		0.780	J	NA		0.036	J	0.102	J	52.9		1.93	
B45-9	4	NA	Puck	1x60	104		0.595	J	NA		0.050	J	0.120	J	51.1		1.77	
B45-10	5	NA	Puck	1x60	114		0.640	J	NA		0.040	J	0.125	J	57.3		1.93	
B45-11	6	NA	Puck	1x60	127		0.660	J	NA		0.050	J	0.110	J	52.0		1.71	
B45-12	7	NA	Puck	1x60	125		0.665	J	NA		0.040	J	0.125	J	59.1		1.81	
B45-13	8	NA	Puck	1x60	131		0.680	J	NA		0.040	J	0.120	J	57.3		1.96	
B45-14	9	NA	Puck	1x60	118		0.641	J	NA		0.040	J	0.111	J	52.5		1.72	
B45-15	10	NA	Puck	1x60	121		0.630	J	NA		0.040	J	0.120	J	55.5		1.92	

Experiment ID	Lab Replicate	Unground	Grinder Type	Ground Time (sec)	Al (mg/kg)	Ba (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
B45-16	11	NA	Puck	1x60	138	0.650	J	0.035	J	51.4	1.79
B45-17	12	NA	Puck	1x60	125	0.660	J	0.040	J	56.8	1.96
B45-18	13	NA	Puck	1x60	110	0.615	J	0.040	J	52.9	1.77
B45-19	14	NA	Puck	1x60	126	0.670	J	0.035	J	57.1	1.91
B45-20	15	NA	Puck	1x60	119	0.655	J	0.035	J	53.8	1.78
B45-21	1	NA	Puck	1x60	28.6	0.220	U	0.035	U	4.04	1.64
B45-22	2	NA	Puck	1x60	36.0	0.280	J	0.030	U	5.08	1.59
B45-23	3	NA	Puck	1x60	30.8	0.245	U	0.025	U	4.09	1.66
B45-24	4	NA	Puck	1x60	30.2	0.195	U	0.015	U	2.92	1.53
B45-25	5	NA	Puck	1x60	27.8	0.225	U	0.020	U	3.68	1.64
B45-26	6	NA	Puck	1x60	25.4	0.215	U	0.020	U	3.33	1.49
B45-27	7	NA	Puck	1x60	26.4	0.205	U	0.030	U	3.57	1.67
B45-28	8	NA	Puck	1x60	22.3	0.200	U	0.025	U	3.02	1.52
B45-29	9	NA	Puck	1x60	30.3	0.245	U	0.030	U	4.37	1.58
B45-30	10	NA	Puck	1x60	36.9	0.230	U	0.015	U	4.01	1.44
B45-31	11	NA	Puck	1x60	28.3	0.210	U	0.045	U	3.79	1.63
B45-32	12	NA	Puck	1x60	25.2	0.195	U	0.020	U	3.08	1.45
B45-33	13	NA	Puck	1x60	26.1	0.220	U	0.030	U	3.57	1.66
B45-34	14	NA	Puck	1x60	30.6	0.205	U	0.025	U	3.52	1.51
B45-35	15	NA	Puck	1x60	32.7	0.235	U	0.025	U	4.96	1.96
B51-3	1	NA	Puck	1x60	0.31	<0.0400	0.447	<0.0400	<0.0400	<0.0400	0.112
B51-4	2	NA	Puck	1x60	0.351	<0.0400	0.464	<0.0400	<0.0400	<0.0400	0.1
B51-5	3	NA	Puck	1x60	0.332	<0.0400	0.426	<0.0400	<0.0400	<0.0400	0.0977

Experiment ID	Lab Replicate	Unground	Grinder Type	Ground Time (sec)	Al (mg/kg)	Ba (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
B51-6	4	NA	Puck	1x60	0.304	<0.0400	0.428	<0.0400	<0.0400	<0.0400	0.0923
B51-7	5	NA	Puck	1x60	0.232	<0.0400	0.46	<0.0400	<0.0400	<0.0400	0.0737
B51-8	6	NA	Puck	1x60	0.304	<0.0400	0.491	<0.0400	<0.0400	<0.0400	0.0727
B51-9	7	NA	Puck	1x60	0.42	<0.0400	0.432	<0.0400	<0.0400	0.0462	0.0636
B51-10	8	NA	Puck	1x60	0.297	<0.0400	0.433	<0.0400	<0.0400	<0.0400	0.0664
B51-11	9	NA	Puck	1x60	0.252	<0.0400	0.393	<0.0400	<0.0400	<0.0400	0.0616
B51-13	11	NA	Puck	1x60	<1.00	<0.400	<1.00	1.4	1.29	3.55	15.5
B51-14	12	NA	Puck	1x60	<1.00	3.9	1.11	<0.400	<0.400	<0.400	<0.400
B51-15	1	NA	Puck	1x60	1.76	<0.400	<1.00	<0.400	<0.400	1.37	<0.400
B51-16	2	NA	Puck	1x60	1.59	<0.0400	0.584	<0.0400	<0.0400	1.4	0.118
B51-17	3	NA	Puck	1x60	1.6	<0.0400	0.577	<0.0400	<0.0400	1.39	0.114
B51-18	1	NA	Puck	2x60	2.23	<0.0400	0.501	<0.0400	<0.0400	2.77	0.119
B51-19	2	NA	Puck	2x60	2.27	<0.0400	0.547	<0.0400	<0.0400	2.22	0.109
B51-20	3	NA	Puck	2x60	2.29	<0.0400	0.534	<0.0400	<0.0400	2.31	0.104
B51-21	1	NA	Puck	3x60	2.74	<0.0400	0.571	<0.0400	<0.0400	3.03	0.104
B51-22	2	NA	Puck	3x60	2.76	<0.0400	0.506	<0.0400	<0.0400	3.04	0.101
B51-23	3	NA	Puck	3x60	2.78	<0.0400	0.506	<0.0400	<0.0400	3.05	0.0987
B51-24	4	NA	Puck	3x60	2.69	<0.0400	0.482	<0.0400	<0.0400	2.93	0.0917
B51-25	5	NA	Puck	3x60	2.78	<0.0400	0.487	<0.0400	<0.0400	2.98	0.127
B51-26	6	NA	Puck	3x60	2.73	<0.0400	0.564	<0.0400	<0.0400	2.99	0.108
B51-27	7	NA	Puck	3x60	2.73	<0.0400	0.48	<0.0400	<0.0400	2.9	0.0975
B51-28	8	NA	Puck	3x60	2.74	<0.0400	0.548	<0.0400	<0.0400	2.95	0.0971

Experiment ID	Lab Replicate	Unground	Grinder Type	Ground Time (sec)	Al (mg/kg)	Ba (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
B51-29	9	NA	Puck	3x60	2.74	<0.0400	0.639	<0.0400	<0.0400	2.98	0.0934
B51-30	10	NA	Puck	3x60	2.78	<0.0400	0.523	<0.0400	<0.0400	2.96	0.089
B51-31	11	NA	Puck	3x60	2.72	<0.0400	0.482	<0.0400	<0.0400	2.93	0.0835
B51-32	12	NA	Puck	3x60	2.73	<0.0400	0.86	<0.0400	<0.0400	2.95	0.0851

Fe (mg/kg)	Mg (mg/kg)	Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)	Pb (mg/kg)		Sb (mg/kg)		K (mg/kg)	Na (mg/kg)		S (mg/kg)		Sr (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)		Comment
3.19	6.48	0.075	U	0.045	U	1.96	0.185	J	0.030	U	NA	NA		NA		0.080	J	-0.020	U	0.215	U	0.685		Unground Glass
2.55	7.94	0.075	U	0.020	U	2.54	0.085	U	0.060	U	NA	NA		NA		0.075	J	-0.020	U	0.100	U	0.520		Unground Glass
3.66	11.5	0.060	U	0.015	U	3.06	0.045	U	0.020	U	NA	NA		NA		0.070	J	-0.025	U	0.075	U	1.28		Unground Glass
684	9.36	5.10		1.14	J	3.92	1.50		1.83		NA	NA		NA		0.195		0.045	J	0.070	U	1.15		Ground Glass
690	9.17	5.11		1.11	J	3.91	1.47	J	1.28	J	NA	NA		NA		0.190		0.045	J	0.035	U	1.56		Ground Glass
692	9.39	5.05		1.13	J	4.30	1.64		1.29	J	NA	NA		NA		0.195		0.065	J	0.705	J	1.39		Ground Glass
1.96	5.73	0.025	U	-0.005	U	2.49	0.070	U	0.030	U	NA	NA		NA		0.050	J	-0.035	U	0.305	U	0.225		Unground Glass, Washed
1.85	5.43	0.020	U	0.005	U	2.77	0.065	U	0.015	U	NA	NA		NA		0.050	J	-0.030	U	0.220	U	0.445		Unground Glass, Washed
1.73	4.99	0.025	U	-0.005	U	2.40	0.055	U	-0.010	U	NA	NA		NA		0.050	J	-0.025	U	0.105	U	0.550		Unground Glass, Washed
50.6	5.09	0.900		3.63		2.77	0.325	J	0.140	J	NA	NA		NA		0.080	J	-0.025	U	0.075	U	0.350		Ground Glass, Washed
51.7	4.84	0.900		3.74		2.83	0.275	J	0.175	J	NA	NA		NA		0.080	J	-0.010	U	0.065	U	0.355		Ground Glass, Washed
49.5	5.40	0.860		3.43		2.93	0.240	J	0.135	J	NA	NA		NA		0.085	J	-0.015	U	0.070	U	0.500		Ground Glass, Washed
433	8.44	J 3.44		0.603	J	1.88	2.08		0.793	J	NA	NA		NA		0.201		0.041	J	-0.103	U	0.912		Ground Glass
426	8.33	J 3.51		0.680	J	1.93	2.79		0.690	J	NA	NA		NA		0.190		0.045	J	-0.145	U	0.830		Ground Glass
400	8.39	J 3.33		0.607	J	1.90	2.96		0.699	J	NA	NA		NA		0.219		0.036	J	-0.179	U	0.770		Ground Glass

Fe (mg/kg)	Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		K (mg/kg)		Na (mg/kg)		S (mg/kg)		Sr (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)		Comment
380	8.24	J	3.10		0.610	J	1.84		1.19	J	0.625	J	NA		NA		NA		0.165		0.045	J	-0.160	U	0.610		Ground Glass
427	8.09	J	3.50		0.770	J	1.89		1.58		0.765	J	NA		NA		NA		0.180		0.040	J	-0.175	U	0.765		Ground Glass
390	7.53	J	3.17		0.545	J	1.97		2.17		0.720	J	NA		NA		NA		0.180		0.035	J	0.115	U	0.860		Ground Glass
435	8.36	J	3.59		0.610	J	2.01		1.95		0.750	J	NA		NA		NA		0.185		0.055	J	-0.025	U	0.860		Ground Glass
422	8.18	J	3.49		0.495	J	2.02		2.12		0.700	J	NA		NA		NA		0.200		0.045	J	-0.090	U	1.265		Ground Glass
389	8.06	J	3.19		0.606	J	1.99		1.74		0.692	J	NA		NA		NA		0.182		0.035	J	-0.126	U	1.21		Ground Glass
412	8.11	J	3.43		0.625	J	2.09		1.89		0.695	J	NA		NA		NA		0.175		0.045	J	-0.130	U	1.005		Ground Glass
391	8.31	J	3.19		0.645	J	2.16		2.67		0.580	J	NA		NA		NA		0.185		0.045	J	-0.185	U	0.785		Ground Glass
430	8.81	J	3.52		0.650	J	2.23		2.02		0.720	J	NA		NA		NA		0.185		0.040	J	-0.170	U	0.985		Ground Glass
390	8.43	J	3.20		0.585	J	2.10		1.33	J	0.690	J	NA		NA		NA		0.175		0.045	J	-0.145	U	0.910		Ground Glass
426	8.14	J	3.47		0.545	J	2.14		1.96		0.720	J	NA		NA		NA		0.185		0.050	J	-0.165	U	1.00		Ground Glass
399	8.24	J	3.25		0.640	J	2.15		1.65		0.660	J	NA		NA		NA		0.180		0.050	J	-0.160	U	0.885		Ground Glass
24.0	4.89	J	0.260	J	0.040	U	1.51		0.520	J	0.075	U	NA		NA		NA		0.080	J	0.010	J	0.100	U	0.450		Ground Glass, Washed
31.7	5.22	J	0.350	J	0.185	J	1.70		0.515	J	0.060	U	NA		NA		NA		0.095	J	0.010	J	0.010	U	0.435		Ground Glass, Washed
25.5	4.83	J	0.280	J	0.100	J	1.59		0.425	J	0.035	U	NA		NA		NA		0.085	J	0.000	U	-0.080	U	0.385		Ground Glass, Washed
16.9	4.72	J	0.210	J	0.200	J	1.62		0.720	J	0.000	U	NA		NA		NA		0.075	J	0.000	U	-0.130	U	0.515		Ground Glass, Washed
21.2	4.56	J	0.245	J	0.050	U	1.55		0.490	J	0.065	U	NA		NA		NA		0.080	J	-0.005	U	-0.120	U	0.605		Ground Glass, Washed
18.4	4.03	J	0.220	J	0.220	J	1.59		0.405	J	0.015	U	NA		NA		NA		0.070	J	-0.010	U	-0.140	U	0.360		Ground Glass, Washed
20.0	4.54	J	0.230	J	0.075	U	1.66		0.465	J	-0.010	U	NA		NA		NA		0.075	J	0.005	U	-0.115	U	0.390		Ground Glass, Washed
16.9	4.41	J	0.210	J	0.180	J	1.56		0.365	J	-0.010	U	NA		NA		NA		0.070	J	-0.010	U	-0.170	U	0.595		Ground Glass, Washed
25.2	4.49	J	0.295	J	0.370	J	1.68		0.390	J	0.015	U	NA		NA		NA		0.075	J	0.010	U	-0.180	U	0.390		Ground Glass, Washed
23.3	4.50	J	0.255	J	0.090	J	1.71		0.780	J	0.050	U	NA		NA		NA		0.080	J	0.005	U	-0.200	U	0.420		Ground Glass, Washed
21.9	4.33	J	0.255	J	0.010	J	1.74		0.495	J	0.015	U	NA		NA		NA		0.075	J	0.020	J	0.110	U	0.260		Ground Glass, Washed

Fe (mg/kg)	Mg (mg/kg)	Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)	Pb (mg/kg)		Sb (mg/kg)		K (mg/kg)	Na (mg/kg)	S (mg/kg)	Sr (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)		Comment				
16.9	3.60	J	0.205	J	0.160	J	1.64		0.455	J	-0.020	U	NA	NA		NA		0.065	J	-0.005	U	-0.055	U	0.220	Ground Glass, Washed	
20.2	4.18	J	0.225	J	0.230	J	1.74		0.470	J	0.025	U	NA	NA		NA		0.075	J	0.010	J	-0.090	U	0.275	Ground Glass, Washed	
19.6	4.33	J	0.210	J	0.140	J	1.63		0.645	J	-0.065	U	NA	NA		NA		0.070	J	0.000	U	-0.120	U	0.435	Ground Glass, Washed	
30.2	4.94	J	0.320	J	0.150	J	1.78		0.480	J	0.015	U	NA	NA		NA		0.085	J	0.000	U	-0.110	U	0.395	Ground Glass, Washed	
0.0957	<0.100		<0.0400		<0.0400		<0.0400		<0.0400		0.59		3.03	<0.0400	NA		<0.0400		<0.0400		<0.0400		<0.0400		Ground 60s, Washed	
0.0973	<0.100		<0.0400		<0.0400		<0.0400		<0.0400		0.65		3.41	<0.0400	NA		<0.0400		<0.0400		0.0673				Ground 60s	
0.124	<0.100		<0.0400		<0.0400		<0.0400		<0.0400		0.581		3.21	<0.0400	NA		<0.0400		<0.0400		<0.0400		<0.0400		Ground 60s	
0.109	<0.100		<0.0400		<0.0400		<0.0400		<0.0400		0.613		3	<0.0400	NA		<0.0400		<0.0400		<0.0400		<0.0400		Ground 60s	
0.0627	<0.100		<0.0400		<0.0400		<0.0400		<0.0400		0.404		2.07	<0.0400	NA		<0.0400		<0.0400		<0.0400		<0.0400		Ground 60s	
0.155	<0.100		<0.0400		<0.0400		<0.0400		<0.0400		0.552		2.92	<0.0400	NA		<0.0400		<0.0400		<0.0400		<0.0400		Ground 60s	
0.108	<0.100		<0.0400		<0.0400		<0.0400		<0.0400		0.768		4.29	<0.0400	NA		<0.0400		<0.0400		<0.0400		<0.0400		Ground 60s	
0.113	<0.100		<0.0400		<0.0400		<0.0400		<0.0400		0.583		2.82	<0.0400	NA		<0.0400		<0.0400		<0.0400		<0.0400		Ground 60s	
0.0618	<0.100		<0.0400		<0.0400		<0.0400		<0.0400		0.394		2.3	<0.0400	NA		<0.0400		<0.0400		<0.0400		<0.0400		Ground 60s	
<0.400	<1.00		<0.400		1.33		3.15		<0.400		2.22		1.34	3.09	69.3	NA		0.706		88.3		4.28			Ground 60s	
<0.400	<1.00		<0.400		<0.400		<0.400		2.28		<0.400		1.35	3.29	<0.400	NA		<0.400		<0.400		<0.400		<0.400		Ground 60s
10.5	<1.00		<0.400		<0.400		<0.400		1.26		<0.400		3.62	14.8	<0.400	NA		<0.400		<0.400		<0.400		<0.400		Ground 60s, washed
10.8	0.119	0.09		<0.0400		<0.0400	<0.0400		<0.0400		3.02		14.6	<0.0400	NA		<0.0400		<0.0400		0.0497				Ground 60s, washed	
10.8	0.116	0.0902		<0.0400		<0.0400	<0.0400		<0.0400		3.05		14.7	0.0419	NA		<0.0400		<0.0400		0.0497				Ground 60s, washed	
21.2	0.121	0.172		<0.0400		<0.0400	<0.0400		<0.0400		4.24		20.3	<0.0400	NA		<0.0400		<0.0400		0.0479				Ground 2x60s, washed	
16.9	0.126	0.137		<0.0400		<0.0400	<0.0400		<0.0400		4.31		20.8	0.0443	NA		<0.0400		<0.0400		0.0457				Ground 2x60s, washed	
17.4	0.115	0.14		<0.0400		<0.0400	<0.0400		<0.0400		4.36		21.2	<0.0400	NA		<0.0400		<0.0400		0.0443				Ground 2x60s, washed	
22.8	0.135	0.183		<0.0400		<0.0400	<0.0400		<0.0400		5.11		24.9	<0.0400	NA		<0.0400		<0.0400		0.0598				Ground 3x60s, washed	

Fe (mg/kg)	Mg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	P (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	K (mg/kg)	Na (mg/kg)	S (mg/kg)	Sr (mg/kg)	V (mg/kg)	W (mg/kg)	Zn (mg/kg)	Comment
23	0.123	0.186	<0.0400	<0.0400	<0.0400	<0.0400	5.11	25	<0.0400	NA	<0.0400	<0.0400	0.042	Ground 3x60s, washed
23.1	0.121	0.184	<0.0400	<0.0400	<0.0400	<0.0400	5.19	24.9	<0.0400	NA	<0.0400	<0.0400	<0.0400	Ground 3x60s, washed
22.5	0.122	0.18	<0.0400	<0.0400	<0.0400	<0.0400	4.96	24.1	<0.0400	NA	<0.0400	<0.0400	<0.0400	Ground 3x60s, washed
22.4	0.131	0.181	<0.0400	<0.0400	<0.0400	<0.0400	5.15	25.1	<0.0400	NA	<0.0400	<0.0400	0.0479	Ground 3x60s, washed
22.3	0.125	0.179	<0.0400	<0.0400	<0.0400	<0.0400	5.09	24.7	<0.0400	NA	<0.0400	<0.0400	0.0402	Ground 3x60s, washed
22	0.119	0.177	<0.0400	<0.0400	<0.0400	<0.0400	5.09	24.6	<0.0400	NA	<0.0400	<0.0400	0.0428	Ground 3x60s, washed
22.2	0.124	0.178	<0.0400	<0.0400	<0.0400	<0.0400	5.14	24.9	<0.0400	NA	<0.0400	<0.0400	0.0419	Ground 3x60s, washed
22.1	0.126	0.177	<0.0400	<0.0400	<0.0400	<0.0400	5.1	24.9	<0.0400	NA	<0.0400	<0.0400	0.0416	Ground 3x60s, washed
22.2	0.129	0.179	<0.0400	<0.0400	<0.0400	<0.0400	5.21	25.2	<0.0400	NA	<0.0400	<0.0400	0.0409	Ground 3x60s, washed
22.3	0.122	0.178	<0.0400	<0.0400	<0.0400	<0.0400	5.07	24.7	<0.0400	NA	<0.0400	<0.0400	0.0411	Ground 3x60s, washed
22.4	0.147	0.181	0.0439	<0.0400	<0.0400	<0.0400	5.01	24.3	<0.0400	NA	<0.0400	<0.0400	0.0582	Ground 3x60s, washed

Table A2. Experiment 2—Grab sample and 10 –increment MI metal results.

Sample ID	Exp. ID	# Inc.	Sampling Approach	Grid Location	Total Mass (g)	< 2mm Mass (g)	> 2mm Mass (g)	Field Rep.	Lab Rep.	Unground	Grinder Type	Ground Time (sec)	Digestion Mass (g)	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	
1D-1	B36-7	1	Grab GN	Grid 1	122.7	NA	NA	NA	1	x	NA	NA	1.00	4373	18.93	0.63	6.73	
1D-2	B36-8	1	Grab GN	Grid 1	122.7	NA	NA	NA	2	x	NA	NA	1.00	4357	18.51	0.63	6.66	
1D-3	B36-9	1	Grab GN	Grid 1	122.7	NA	NA	NA	3	x	NA	NA	1.00	4383	21.13	0.64	6.86	
1D-4	B36-10	1	Grab GN	Grid 1	122.7	NA	NA	NA	4	x	NA	NA	2.00	4260	16.745	0.855	6.335	
1D-5	B36-11	1	Grab GN	Grid 1	122.7	NA	NA	NA	5	x	NA	NA	2.00	4418	16.69	0.855	6.475	
2D	B36-12	1	Grab GN	Grid 2	133.0	NA	NA	NA	NA	x	NA	NA	1.00	3784	20.16	1.13	6.31	
3D	B36-13	1	Grab GN	Grid 3	137.0	NA	NA	NA	NA	x	NA	NA	1.00	4176.9	22.848	0.7038	7.0584	
4D	B36-14	1	Grab GN	Grid 4	133.6	NA	NA	NA	NA	x	NA	NA	1.00	4066.26	17.4326	0.6868	6.7872	
5D	B36-15	1	Grab GN	Grid 5	158.9	NA	NA	NA	NA	x	NA	NA	1.00	4214	20.37	0.78	7.76	
6D	B36-16	1	Grab GN	Grid 6	147.3	NA	NA	NA	NA	x	NA	NA	1.00	4449	39.45	0.73	7.17	
7D	B36-17	1	Grab GN	Grid 7	151.5	NA	NA	NA	NA	x	NA	NA	1.00	4117	30.73	1	8.38	
8D	B36-18	1	Grab GN	Grid 8	157.1	NA	NA	NA	NA	x	NA	NA	1.00	4087	26.64	0.68	6.77	
9D	B36-19	1	Grab GN	Grid 9	144.5	NA	NA	NA	NA	x	NA	NA	1.00	4224	21.25	0.68	7.33	
10D	B36-20	1	Grab GN	Grid 10	150.6	NA	NA	NA	NA	x	NA	NA	1.00	4158	17.01	0.78	7.1	
11D	B36-21	1	Grab GN	Grid 11	157.2	NA	NA	NA	NA	x	NA	NA	1.00	4360	19.44	0.81	7.42	
12D	B36-22	1	Grab GN	Grid 12	139.6	NA	NA	NA	NA	x	NA	NA	1.00	4115	17.03	0.83	7.64	
13D	B36-23	1	Grab GN	Grid 13	143.6	NA	NA	NA	NA	x	NA	NA	1.00	4255.13	17.1801	0.6565	7.0498	
14D	B36-24	1	Grab GN	Grid 14	144.2	NA	NA	NA	NA	x	NA	NA	1.00	4283	27.22	0.82	7.63	
15D	B36-25	1	Grab GN	Grid 15	146.6	NA	NA	NA	NA	x	NA	NA	1.00	4328	18.03	0.85	7.8	
16D	B36-26	1	Grab GN	Grid 16	151.9	NA	NA	NA	NA	x	NA	NA	1.00	4087	31.1	0.67	6.88	
17D	B36-27	1	Grab GN	Grid 17	149.1	NA	NA	NA	NA	x	NA	NA	1.00	4417	18.42	0.79	7.97	
18D	B36-28	1	Grab GN	Grid 18	141.9	NA	NA	NA	NA	x	NA	NA	1.00	4173	17.31	0.72	7.71	
19D	B36-29	1	Grab GN	Grid 19	147.4	NA	NA	NA	NA	x	NA	NA	1.00	4103	15.75	0.69	7.02	
20D	B36-30	1	Grab GN	Grid 20	148.8	NA	NA	NA	NA	x	NA	NA	1.00	4296	17.86	0.76	7.41	
21D	B36-31	1	Grab GN	Grid 21	140.0	NA	NA	NA	NA	x	NA	NA	1.00	4253	17.17	0.76	7.76	
22D	B36-32	1	Grab GN	Grid 22	147.0	NA	NA	NA	NA	x	NA	NA	1.00	4058	15.99	0.73	7.47	
23D	B36-33	1	Grab GN	Grid 23	154.0	NA	NA	NA	NA	x	NA	NA	1.00	4324	17.33	0.71	7.69	
24D	B36-34	1	Grab GN	Grid 24	151.7	NA	NA	NA	NA	x	NA	NA	1.00	4238	15.72	0.74	7.46	
25D	B36-35	1	Grab GN	Grid 25	142.2	NA	NA	NA	NA	x	NA	NA	1.00	3940	16.34	0.62	6.97	
26D	B36-36	1	Grab GN	Grid 26	139.7	NA	NA	NA	NA	x	NA	NA	1.00	4577	17.91	0.82	8.11	

Sample ID	Exp. ID	# Inc.	Sampling Approach	Grid Location	Total Mass (g)	< 2mm Mass (g)	> 2mm Mass (g)	Field Rep.	Lab Rep.	Unground	Grinder Type	Ground Time (sec)	Digestion Mass (g)	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)
27D	B36-37	1	Grab GN	Grid 27	125.9	NA	NA	NA	NA	x	NA	NA	1.00	4321	16.96	0.68	7.73
28D	B36-38	1	Grab GN	Grid 28	132.1	NA	NA	NA	NA	x	NA	NA	1.00	4202	16.1	0.67	7.77
29D	B36-39	1	Grab GN	Grid 29	121.5	NA	NA	NA	NA	x	NA	NA	1.00	4275	17.01	0.75	7.93
30D	B36-40	1	Grab GN	Grid 30	158.0	NA	NA	NA	NA	x	NA	NA	1.00	4278	17.1	0.71	7.3
31D	B36-41	1	Grab BR	Grid 15	156.4	NA	NA	NA	NA	x	NA	NA	1.00	4412	17.86	0.96	7.47
32D	B36-42	1	Grab BR	Grid 22	149.7	NA	NA	NA	NA	x	NA	NA	1.00	4131	16.02	0.52	6.56
33D	B36-43	1	Grab BR	Grid 30	147.3	NA	NA	NA	NA	x	NA	NA	1.00	4184	16.03	0.64	7.21
34D	B36-44	1	Grab BR	Grid 7	153.7	NA	NA	NA	NA	x	NA	NA	1.00	4065	14.6	0.58	6.83
35D	B36-45	1	Grab BR	Grid 6	146.9	NA	NA	NA	NA	x	NA	NA	1.00	4206	17.58	0.58	6.84
36D	B36-46	1	Grab BR	Grid 23	138.7	NA	NA	NA	NA	x	NA	NA	1.00	3968	15.2	0.6	6.9
38-R1	B43-7	100	MI SR	NA	1176.6	1153.9	21.8	1	1	NA	Puck	5x60	2.00	6055	34.05	0.89	9.535
38-R2	B43-8	100	MI SR	NA	1176.6	1153.9	21.8	1	2	NA	Puck	5x60	2.00	6385	34.485	0.91	9.61
38-R3	B43-9	100	MI SR	NA	1176.6	1153.9	21.8	1	3	NA	Puck	5x60	2.00	6595	33.72	0.965	9.625
39	B43-10	100	MI SR	NA	1295.1	1264.6	28.8	2	NA	NA	Puck	5x60	2.00	6745	32.875	0.98	9.625
40	B43-11	100	MI SR	NA	1361.4	1340.0	20.2	3	NA	NA	Puck	5x60	2.00	6540	31.325	0.985	9.46
41	B43-12	100	MI SR	NA	1419.3	1393.8	24.3	4	NA	NA	Puck	5x60	2.00	6380	30.17	0.94	9.31
42	B43-13	100	MI SR	NA	1991.6	1948.6	41.2	5	NA	NA	Puck	5x60	2.00	6335	29.765	0.95	9.26
43	B43-14	100	MI SR	NA	1801.3	1750.7	47.9	6	NA	NA	Puck	5x60	2.00	6155	30.72	0.955	9.095
44	B43-15	100	MI SR	NA	1725.4	1679.2	45.3	7	NA	NA	Puck	5x60	2.00	6420	30.52	0.965	9.33

Cr (mg/kg)	Cu (mg/kg)	Fe (mg/kg)	Mg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	P (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Sr (mg/kg)	V (mg/kg)	W (mg/kg)	Zn (mg/kg)
5.84	210.9	11340	1966	192.6	9.1	520.8	1276	9.14	8.76	9.78	0.64	U 60.45
5.96	223.1	11340	2011	192.9	9.59	559	1136	9.36	8.92	9.74	0.55	U 60.29
5.74	223.3	11350	1989	188.9	9.17	544.5	1417	9.67	9.13	10.08	1.26	J 60.18
5.8	248.1	9880	1909.5	183.95	9.06	635.5	4146.5	47.03	9.67	10.03	0.825	J 59
5.83	218.3	9975	1968.5	183.7	9.125	582	1263.5	7.865	9.97	9.975	0.685	J 57.4
6.1	473.4	11590	2025	194.8	10.06	467.8	79020	2072	16.31	9.14	0.89	J 82.16
6.0384	135.762	11954.4	2324.58	224.706	10.0062	497.454	43.9212	0.8976	J 22.7766	9.843	0.59	U 44.676

Cr (mg/kg)		Cu (mg/kg)		Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)
5.6863		262.903		11948.3		1752.35		177.154		9.6152		781.639		2349.26		21.6544		9.9687		11.1403		0.7	U	56.8428
6.65		453.6		12860		2128		204.3		10.41		582.8		5328		73.72		13.16		11.84		0.91	J	92.56
6.28		208.7		12200		2257		221.4		10.22		586.2		691.8		5.26		16.9		10.15		0.62	U	60.59
6.99		247.5		14700		1877		196.6		9.93		1043		4858		27.81		11.38		15.35		0.6	U	60.7
6.04		514.5		11790		1997		190.2		10.12		576.6		9235		82.46		13.36		9.97		0.81	J	90.24
5.67		316.4		11930		2026		241.8		9.63		623.4		1213		10.13		12.15		10.34		1.37	J	69.35
6.26		349.5		12720		1953		192.1		9.8		744.6		2840		30.55		10.1		11.45		1.09	J	73.9
6.88		597.7		12610		2032		214.3		10.72		685.6		3537		30.33		13.46		11.68		1.21	J	110.5
6.25		534.4		12720		1954		184.4		10.09		816.6		1767		12.95		12.06		12.05		1.02	J	91.62
5.8479		357.237		11806.9		2047.27		190.284		9.8576		661.348		986.366		7.2215		10.7969		10.2818		0.7777	U	70.9929
6.35		413.5		13130		1997		201.1		10.31		726.2		1952		18.08		11.59		11.63		0.82	J	79.83
6.91		360.6		13520		1999		197.3		10.25		832.1		2623		23.55		11.37		12.91		0.74	U	74.61
5.7		225.5		11930		1815		177.4		9.08		724.7		808.6		5.61		10.55		10.94		0.56	U	55.1
6.84		325.6		12850		2076		204.4		10.25		718.3		1060		8.24		16.02		11.71		0.7	U	70.72
6.06		69.82		12230		1965		197.5		10.01		724.1		217		1.97	J	13.05		10.58		0.4	U	35.81
5.85		211.1		12000		1815		183.3		9.63		690.2		1977		30.28		9.86		10.35		1.19	J	53.99
6.13		454.3		12440		1914		198.6		9.95		681.7		19038		75.97		10.34		11.29		1.18	J	89.66
6.28		243.6		12600		2040		220		10.15		720.5		2868		24.69		14.27		11.94		0.8	J	60.43
6.09		251.8		12630		1882		178.4		9.28		734.4		1204		9.89		11.99		11.81		0.75	U	60.41
6.36		162.5		12320		1871		193.4		9.75		813.4		318.9		2.69	J	11.6		11.47		0.49	U	47.61
6.11		313.4		12590		1937		186.7		9.94		757.9		1061		7.55		12.02		11.47		0.67	U	65.29
5.58		162		11500		1748		174.8		8.67		766.3		351.5		2.41	J	11.26		10.63		0.49	U	43.52
6.37		277.2		13460		2036		206.6		10.5		865.8		2307		13.95		15.07		12.81		0.63	U	63.12
6.77		225.2		12090		1961		187.3		10.04		687.9		867.5		8.26		13.31		10.79		0.58	U	54.05
6.47		92.87		12140		1934		194.9		9.79		741.3		126.9		1.43	J	15.45		10.98		0.43	U	38.4
6.55		317.6		12710		2001		201.1		10.26		834.9		938		7.83		14.17		11.7		1.35	J	72.09
5.59		217.3		12490		1960		196		9.96		622.5		950.5		9.26		12.45		10.98		0.92	U	55.74
6.86		270		13180		2062		207		10.47		803.7		1930		16.39		12.23		12.38		0.8	J	63.38
5.58		224.4		10800		1934		179.4		9.29		546.1		500.9		3.48		10.09		8.75		0.66	U	57.6
5.95		215.5		11810		1937		199.8		9.7		668.4		555.3		4.17		11.86		10.04		0.64	U	55.02
5.97		280		11090		1805		173.2		8.87		783.2		1650		11.9		10.7		9.88		0.65	U	61.2

Cr (mg/kg)		Cu (mg/kg)		Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)
5.2		392.1		11070		1922		189.9		8.92		532.1		1851		24.06		14.33		8.85		0.69	U	67.04
5.56		229.3		11660		1734		178.5		8.74		815.9		478.6		5.68		12.45		10.35		0.51	U	52.1
337.6		551		17840	D	2257		248.2		12.865		721		2406		19.605		23.26		16.675		0.315	U	86.35
340.45		467.25		17760	D	2251.5		251.05		12.84		733		2529		20.355		24.69		17.13		0.26	U	71.8
337.8		552.5		16980	D	2201		247.35		12.785		736		2489.5		19.755		25.74		17.275		0.205	U	74.9
311.3		412.5		19200	D	2243		254.1		12.98		748.5		2538.5		19.545		26.17		17.03		0.185	U	65.2
292.95		739		18850	D	2188.5		245.75		12.785		779		3594.5		28.855		25.515		16.84		0.345	U	94.8
281.7		528.5		18515	D	2130.5		236.1		12.35		767.5		2638		20.17		24.54		16.71		0.14	U	72.3
275.8		814.5		18390	D	2191.5		245.9		12.545		762		3108.5		24.04		24.475		15.95		0.25	U	91.15
288		881.5		17695	D	2205.5		242.25		13.175		754.5		3564		26.89		24.31		15.985		0.42	J	95.9
286.25		609		18067	D	2175		243.4		12.37		751		2569		20.655		26.695		16.34		0.25	U	78.2

Table A3. Experiment 3—Multi-increment sample metal results.

Sample ID	Exp ID	# Inc	Total Mass (g)	< 2mm Mass (g)	> 2mm Mass (g)	Field Rep	Lab Rep	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
45	B37-7	5	1100.9	1059.7	40.5	1	NA	6250	30.035	1.205	8.99	237.5	323.2
46	B37-10	5	875.0	848.7	25.2	2	NA	6425	30.715	1.26	9.41	290.3	456.35
47	B37-11	5	872.9	861.5	10.8	3	NA	6040	28.565	1.11	8.655	284.8	639.5
48	B37-12	5	1033.6	1004.1	28.4	4	NA	6120	28.585	1.075	8.805	247.3	641
49	B37-13	5	1068.8	1040.5	25.4	5	NA	6135	27.65	1.095	8.605	247.3	534.5
50	B37-14	5	1209.8	1143.5	63.2	6	NA	6155	28.37	1.085	8.42	234.95	526
51	B37-15	5	1331.6	1277.3	51.5	7	NA	6485	29.975	1.265	9.075	290.1	649.5
52	B37-16	50	622.6	616.7	5.5	1	NA	6550	30.18	1.18	9.135	370	352.5
53	B37-17	50	643.5	631.0	10.0	2	NA	6730	31.625	1.17	9.035	358.25	408.7
54	B37-18	50	630.9	621.6	6.9	3	NA	6770	32.045	1.145	9.055	372.75	349.1
55-Rep 1	B37-19	50	345.7	333.8	6.0	4	1	6790	30.965	1.205	9.255	365.25	558
55-Rep 2	B37-20	50	345.7	333.8	6.0	4	2	6785	30.905	1.185	9.265	368.5	509.5
55-Rep 3	B37-21	50	345.7	333.8	6.0	4	3	6780	31.045	1.21	9.32	366.1	444.05
56	B37-22	50	372.9	366.6	4.1	5	NA	6560	30.61	1.2	9.12	329.65	431.3
57	B37-23	50	344.0	337.3	4.4	6	NA	6130.2	25.9743	1.1526	8.7312	228.327	582.93
58	B37-24	50	609.5	593.2	13.7	7	NA	6695	29.875	1.29	9.74	361.1	516
59	B37-25	30	320.4	309.3	8.9	1	NA	6960	30.89	1.18	9.145	345.25	518
60	B37-26	30	305.2	291.8	11.2	2	NA	7160	31.5	1.26	9.43	441.85	557
61	B37-27	30	303.3	299.0	2.1	3	NA	7105	31.095	1.22	9.355	389.65	554
62	B37-28	30	304.7	295.2	7.7	4	NA	7370	31.37	1.41	9.85	389.5	532
63	B37-29	30	274.1	264.3	7.6	5	NA	7510	32.41	1.39	9.925	398.75	762.5

Sample ID	Exp ID	# Inc	Total Mass (g)	< 2mm Mass (g)	> 2mm Mass (g)	Field Rep	Lab Rep	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
64	B37-30	30	277.1	264.0	10.9	6	NA	7475	31.7	1.37	9.94	411.55	527.5
65-Rep 1	B37-31	30	351.8	332.1	13.6	7	1	6985	29.6	1.28	9.245	388.3	562
65-Rep 2	B37-32	30	351.8	332.1	13.6	7	2	6573.9	38.4183	1.071	9.5523	426.411	471.138
65-Rep 3	B37-33	30	351.8	332.1	13.6	7	3	6630	38.165	1.11	9.55	432.55	560
66	B37-35	20	194.9	183.9	9.0	1	NA	7580	47.11	1.21	10.2	513	529.5
67	B37-36	20	198.9	195.8	1.2	2	NA	7640	46.845	1.23	10.29	572.5	688.5
68	B37-37	20	242.5	239.4	1.1	3	NA	7200	42.165	1.12	9.645	415	539.5
69	B37-38	20	128.3	125.2	1.0	4	NA	4659.5	18.915	0.63	6.79	22.395	330.4
70	B37-39	20	143.3	138.1	3.4	5	NA	4666.5	19.065	0.67	6.76	6.615	426.1
71	B37-40	20	137.9	128.6	7.2	6	NA	4465	17.46	0.6	6.47	6.29	363.2
72	B37-41	20	157.7	154.9	0.8	7	NA	4559	17.5	0.665	6.69	6.2	430.9
73	B37-42	10	88.6	86.4	0.4	1	NA	4337	16.46	0.57	6.61	5.865	447.8
74	B37-43	10	104.4	98.9	3.6	2	NA	4443.12	16.5546	0.6324	6.5892	6.3903	405.807
75-Rep 1	B37-44	10	83.4	76.4	1.0	3	1	4619	17.665	0.705	6.965	6.64	591.5
75-Rep 2	B37-45	10	83.4	76.4	1.0	3	2	4439	16.375	0.65	6.745	6.18	416.6
75-Rep 3	B37-46	10	83.4	76.4	1.0	3	3	4465	16.405	0.635	6.775	6.43	431.35
76	B37-47	10	154.1	150.8	1.3	4	NA	4400.5	16.355	0.685	6.69	5.85	5930
77	B37-48	10	171.9	168.9	1.1	5	NA	4383	15.85	0.595	6.56	5.815	326.5
78	B38-18	10	150.4	147.5	1.0	6	NA	3821.5	15.88	1.035	6.745	6.215	287.45
79	B38-19	10	92.6	90.2	0.4	7	NA	3673	15.24	1.02	6.325	5.765	948
CEA37	B39-26	200	20846.8	20408	438.9	NA	1	5490	32.02	1.845	8.765	232.9	503
CEA37	B39-27	200	20846.8	20408	438.9	NA	2	5545	33.3	1.85	8.84	232.45	492

Sample ID	Exp ID	# Inc	Total Mass (g)	< 2mm Mass (g)	> 2mm Mass (g)	Field Rep	Lab Rep	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
CEA37	B39-28	200	20846.8	20408	438.9	NA	3	5585	32.12	1.86	8.935	229	391.25
CEA37	B39-29	200	20846.8	20408	438.9	NA	4	5605	32.305	1.835	8.81	228.75	540.5
CEA37	B39-30	200	20846.8	20408	438.9	NA	5	5505	31.695	1.8	8.82	224.8	416.75
CEA37	B39-31	200	20846.8	20408	438.9	NA	6	5505	31.835	1.8	8.74	231.05	517
CEA37	B39-32	200	20846.8	20408	438.9	NA	7	5425	31.32	1.795	8.79	229.95	573.5
CEA37	B39-33	200	20846.8	20408	438.9	NA	8	5450	31.465	1.8	8.715	231.65	472.5
CEA37	B39-34	200	20846.8	20408	438.9	NA	9	5435	31.165	1.785	8.72	227.45	635.5
CEA37	B39-35	200	20846.8	20408	438.9	NA	10	5485	31.485	1.835	8.835	223.2	424.9
CEA37	B39-36	200	20846.8	20408	438.9	NA	11	5485	30.395	1.835	8.75	233.3	585.5
CEA37	B39-37	200	20846.8	20408	438.9	NA	12	5475	30.325	1.83	8.67	236.25	570
CEA37	B39-38	200	20846.8	20408	438.9	NA	13	5520	30.275	1.815	8.75	232.65	461.5
CEA37	B39-39	200	20846.8	20408	438.9	NA	14	5505	29.42	1.815	8.635	221.6	457.85
CEA37	B39-40	200	20846.8	20408	438.9	NA	15	5615	34.8	1.785	8.455	221.65	394.25
CEA37	B40-8	200	20846.8	20408	438.9	NA	16	5840	30.46	1.8	8.66	218.85	601
CEA37	B40-9	200	20846.8	20408	438.9	NA	17	5770	30.3	1.8	8.575	220.85	544.5
CEA37	B40-10	200	20846.8	20408	438.9	NA	18	5740	29.53	1.77	8.405	218.4	485.75
CEA37	B40-11	200	20846.8	20408	438.9	NA	19	5850	29.465	1.805	8.455	218.55	564
CEA37	B40-12	200	20846.8	20408	438.9	NA	20	6010	29.305	1.825	8.48	217.15	540
CEA37	B40-13	200	20846.8	20408	438.9	NA	21	6045	29.125	1.8	8.365	216.4	802
CEA37	B40-14	200	20846.8	20408	438.9	NA	22	6065	28.62	1.82	8.36	216.55	703.5
CEA37	B40-15	200	20846.8	20408	438.9	NA	23	6235	28.82	1.865	8.565	218.4	813
CEA37	B40-16	200	20846.8	20408	438.9	NA	24	6205	28.41	1.83	8.39	218	517.5

Sample ID	Exp ID	# Inc	Total Mass (g)	< 2mm Mass (g)	> 2mm Mass (g)	Field Rep	Lab Rep	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
CEA37	B40-17	200	20846.8	20408	438.9	NA	25	6195	27.45	1.86	8.38	215.95	551.5
CEA37	B40-18	200	20846.8	20408	438.9	NA	26	6185	27.59	1.835	8.325	216.1	636
CEA37	B40-19	200	20846.8	20408	438.9	NA	27	6250	27.135	1.87	8.365	214.75	572
CEA37	B40-20	200	20846.8	20408	438.9	NA	28	6195	28.16	1.825	8.295	213.9	535
CEA37	B40-21	200	20846.8	20408	438.9	NA	29	6455	26.025	1.895	8.325	213.95	592.5
CEA37	B40-22	200	20846.8	20408	438.9	NA	30	6800	25.92	1.945	8.315	216.1	611.5

Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)	
16470	D	2166.5		225.6		12.315		814		2368.5		20.5		20.15		16.16		0.755	J	65.5	
17970	D	2114.5		234.35		13.12		774		2902		23.19		21.24		17.395		0.81	J	75.35	
16470	D	1989.5		208.3		12.3		695.5		2496		19.985		20.76		15.69		0.915	J	85.8	
16955	D	2060.5		215.8		11.96		711		2284		16.845		20.635		15.46		1.165	J	83.15	
17075	D	2023		210.5		12.075		721		2796.5		21.05		20.995		15.515		1	J	78.1	
16705	D	2196		219.95		12.195		593		3885.5		28.94		41.11		14.4		1.005	J	84	
17945	D	2064.5		225.25		12.57		778.5		4187		34.18		24.805		17		0.985	J	85.9	
17845	D	2007		220.75		13.26		735		2346.5		19.56		21.535		16.35		0.74	J	62.35	
16790	D	2010.5		222.5		12.91		714		2003.5		16.965		22.925		17.055		0.77	J	64.25	
14895	D	2032		224.35		12.91		689		1834.5		15.015		23.58		16.955		0.705	J	58.15	
17965	D	2049.5		226.95		13.495		738		2005		16.53		23.64		17.405		0.77	J	73.9	

Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)	
17530	D	2064		228.15		13.23		740.5		1954		16.725		23.58		17.37		0.865	J	78.7	
17740	D	2046.5		226.85		13.27		747.5		1986.5		16.44		23.76		17.455		0.77	J	70.15	
14465	D	2026		223.75		12.955		730.5		2036.5		16.815		22.94		16.795		1	J	65.45	
14499.3	D	2028.78		216.495		12.1023		771.63		2421.48		18.0591		21.5577		15.402		0.9639	J	76.5	
15160	D	1994.5		219.55		13.735		783		2446.5		20.45		25.47		18.655		0.935	J	70	
17650	D	1977.5		220.5		12.885		767.5		2727.5		23.53		24.795		17.575		0.905	J	69.15	
16910	D	1975		223.5		13.675		742		2646.5		22.32		25.545		17.865		0.835	J	70	
16980	D	1977.5		223.2		13.35		761		2784		24.355		25.28		17.93		0.905	J	73.1	
16060	D	2036		237.4		13.775		837		3122		26.71		27.04		19.355		0.83	J	65.4	
20405	D	2030		239.5		13.79		831.5		2435		19.055		27.625		20.2		0.805	J	67.75	
18845	D	2008.5		235.3		13.95		847		2939		25.155		28.235		19.785		0.88	J	67.15	
15195	D	1940		219.65		13.33		758		1993		17.465		26.335		17.53		0.73	J	60.45	
15728.4	D	2419.44		270.198		14.484		680.34		2255.73		17.2329		20.6907		17.0748		0.3417	U	75.531	
17005	D	2412		271.25		14.505		687.5		2174		16.36		20.67		17.335		0.23	U	83.4	
19130	D	2520.5		283.7		15.735		682		3586.5		29		24.285		19.6		0.24	U	91.7	
18785	D	2476		286.75		15.86		683.5		2786		22.885		24.88		19.73		0.16	U	97.4	
17300	D	2401		267.2		14.465		690		2476.5		20.48		23.135		18.39		0.16	U	88.95	
11715	D	2109.5		196		17.505		712.5		1102.5		5.825		13.575		11.005		0.215	U	66.3	
12870	D	2141.5		202.7		9.73		740		3491		43.645		13.56		10.88		0.53	J	76.15	
12640	D	2137		194.9		9.435		738.5		2761.5		21.645		12.93		10.095		0.255	U	68.1	
12595	D	2102.5		210.55		9.685		740.5		2620		17.89		12.795		10.465		0.265	U	76.45	
11915	D	2008		189.7		9.135		724.5		2102.5		19.54		12.215		9.535		0.165	U	77.75	

Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)	
12663.3	D	1995.63		197.166		9.3891		804.27		1441.26		8.1396		12.9897		10.4652		0.2346	U	74.052	
13135	D	2016		198.7		9.59		827		2219		13.415		12.795		10.965		0.15	U	95	
12810	D	2003.5		192.6		9.32		776.5		1917		14.56		11.535		10.6		0.14	U	72	
13540	D	2003.5		193.75		9.455		827.5		1431		7.35		12.375		10.745		0.14	U	72.4	
12580	D	1970.5		200.6		9.825		748.5		3067		23.165		14.59		9.915		-0.025	U	865	
12390	D	1983.5		188.3		9.115		808.5		1814.5		15.475		12.86		9.97		0.2	U	64.2	
12525	D	2004.5		187.85		9.225		563		1333.5		8.075		11.325		9.81		0.32	U	63.35	
11465	D	1931		180.45		8.82		568		2947.5		41.48		10.655		9.78		0.375	U	109.3	
16565	D	2269.5		237.45		12.405		570.5		2779		21.8		20.635		15.255		0.54	J	83.7	
16120	D	2283.5		239.65		12.425		578		2818		22.675		20.98		15.42		0.35	U	80.35	
16955	D	2289.5		239.8		12.475		588.5		2775.5		22.2		20.885		15.595		0.32	U	72.15	
16475	D	2286		239.85		12.41		580.5		2699		20.55		21.15		15.495		0.29	U	83.35	
16095	D	2242		234.9		12.32		583		2859		22.885		20.625		15.315		0.275	U	74.45	
16650	D	2256.5		235.15		12.395		584		2818		22.72		20.535		15.285		0.28	U	85.1	
16995	D	2249.5		234.2		12.43		587		2657		20.905		20.33		15.08		0.31	U	92.85	
17175	D	2255.5		235.75		12.57		590.5		2606.5		20.855		20.305		15.12		0.235	U	80.1	
16150	D	2255		234.35		12.415		589		2779		22.32		20.1		14.995		0.245	U	90.45	
17620	D	2265		237.6		12.49		599.5		2936		22.2		20.305		15.385		0.215	U	74.7	
17165	D	2233.5		234.5		12.48		591		2689.5		21.025		20.505		15.07		0.37	U	85.2	
17170	D	2219.5		234.4		12.52		600		2678.5		19.89		21.17		15.085		0.41	J	93.5	
14775	D	2214.5		233.5		12.42		602		2865.5		22.61		20.605		15.16		0.275	U	78.5	
16915	D	2176		229		12.325		610		2927		24.92		20.59		14.925		0.305	U	73.85	

Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)	
17320	D	2141		224.9		12.155		597		2509		18.905		20.96		14.73		0.21	U	67	
16565	D	2080.5		221.6		11.95		614.5		2487.5		20.345		22.325		15.54		0.285	U	76.5	
16230	D	2100		222.85		11.995		621		2648.5		22.48		21.855		15.275		0.265	U	83.2	
17135	D	2064		220.3		11.88		614.5		2738		22.415		22.015		15.065		0.24	U	70.6	
16925	D	2061.5		220.6		11.89		618.5		2788		23.785		22.285		15.375		0.5	J	75.5	
16505	D	2009		217.2		11.835		623.5		2439.5		21.58		23.175		15.47		0.3	U	69.2	
16505	D	2017		215.1		11.81		621.5		2706.5		24.045		22.975		15.045		0.295	U	82.65	
16725	D	1995.5		214.1		11.89		623.5		2674		23.9		23.41		15.09		0.27	U	76.1	
15530	D	2009		216.5		12.08		631.5		2779		23.655		23.735		15.36		0.31	U	92.65	
17170	D	1987		213.4		11.815		634		2751		24.44		23.745		15.315		0.235	U	65.65	
17505	D	1970.5		211.65		12.71		643.5		2546		22.615		23.96		14.995		0.215	U	67.55	
17080	D	1994		212.75		11.94		637.5		2682		23.81		23.7		14.955		0.16	U	70.55	
17715	D	1966		210.8		11.99		646		2705.5		23.83		23.91		14.99		0.23	U	72.55	
16605	D	2029		217.9		11.755		634.5		2752.5		23.955		23.59		14.725		0.195	U	65.3	
17285	D	1925.5		206.25		11.855		650		2729.5		24.19		24.715		14.99		0.395	U	67.15	
16940	D	1904.5		205		11.815		655		2671.5		25.545		26.25		15.3		0.3	U	64.65	

Table A4. Experiment 4—Cone-and-quartering metal results.

Sample ID	Exp ID	Lab Rep	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	
CEA 1-36, Quarter 1	B49-28	1	6615	26.665	0.59	7.66	187.4	421.4	
CEA 1-36, Quarter 1	B49-29	2	6725	26.94	0.58	7.66	188.15	421.3	
CEA 1-36, Quarter 1	B49-30	3	5710	30.625	0.94	8.635	206.4	392.1	
CEA 1-36, Quarter 1	B49-31	4	5590	30.5	0.52	7.995	199.85	658	
CEA 1-36, Quarter 1	B49-32	5	5480	29.275	0.525	7.785	193.3	365.6	
CEA 1-36, Quarter 1	B49-33	6	5610	29.335	0.525	7.825	196.25	419.9	
CEA 1-36, Quarter 1	B49-34	7	5685	29.31	0.5	7.845	195.1	436.9	
CEA 1-36, Quarter 1	B49-35	8	5665	29.525	0.525	7.755	192.15	528	
CEA 1-36, Quarter 1	B49-36	9	5750	29.42	0.515	7.865	192.55	476.35	
CEA 1-36, Quarter 1	B49-37	10	5802.45	28.7345	0.51005	7.72145	192.4555	381.5275	
CEA 1-36, Quarter 2	B49-38	1	5940	28.165	0.49	7.29	160.75	329.7	
CEA 1-36, Quarter 2	B49-39	2	6060	27.66	0.49	7.315	169.6	334.3	
CEA 1-36, Quarter 2	B49-40	3	6005	27.445	0.49	7.64	169	345.15	
CEA 1-36, Quarter 2	B49-41	4	6580	41.44	0.555	8.405	188.05	398.1	
CEA 1-36, Quarter 2	B49-42	5	5500	26.91	0.845	7.775	172.7	302.75	
CEA 1-36, Quarter 2	B49-43	6	5905	26.645	0.87	7.85	176.1	328.1	
CEA 1-36, Quarter 2	B49-44	7	6095	25.835	0.895	7.695	171.05	335.45	
CEA 1-36, Quarter 2	B49-45	8	6370	25.14	0.925	7.825	171.3	361.8	
CEA 1-36, Quarter 2	B49-46	9	6345	24.82	0.91	7.86	172.5	355.35	
CEA 1-36, Quarter 2	B49-47	10	6305	25.045	0.92	7.4	172.45	357.35	
CEA 1-36, Quarter 3	B49-48	1	6560	24.82	0.91	7.87	178.3	428	
CEA 1-36, Quarter 3	B50-6	2	6440	28.01	0.91	8.095	179.85	367.5	

Sample ID	Exp ID	Lab Rep	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
CEA 1-36, Quarter 3	B50-7	3	6515	26.58	0.9	7.875	175.55	413.05
CEA 1-36, Quarter 3	B50-8	4	6840	26.695	0.905	8.03	178.65	559.5
CEA 1-36, Quarter 3	B50-9	5	6790	26.065	0.905	7.93	176.6	439.4
CEA 1-36, Quarter 3	B50-10	6	6790	25.935	0.915	7.935	177.25	543
CEA 1-36, Quarter 3	B50-11	7	6860	26.53	0.92	7.915	176.6	487.3
CEA 1-36, Quarter 3	B50-12	8	6525	25.285	0.9	7.82	174.55	447.5
CEA 1-36, Quarter 3	B50-13	9	6710	25.745	0.915	7.91	179.7	586.5
CEA 1-36, Quarter 3	B50-14	10	6840	25.195	0.915	7.855	173.75	402.4
CEA 1-36, Quarter 4	B50-15	1	6796.5	23.67275	0.93725	8.10175	174.34	879.75
CEA 1-36, Quarter 4	B50-16	2	7075	25.17	0.965	8.09	179.05	454.25
CEA 1-36, Quarter 4	B50-17	3	7065	24.935	1	8.035	180.1	1189.5
CEA 1-36, Quarter 4	B50-18	4	6860	24.32	0.965	7.94	176.9	456.8
CEA 1-36, Quarter 4	B50-19	5	6605	23.745	0.95	7.84	173.1	459.35
CEA 1-36, Quarter 4	B50-20	6	6660	23.75	0.965	7.945	176.8	597
CEA 1-36, Quarter 4	B50-21	7	6800	23.645	0.96	7.975	174.05	493.9
CEA 1-36, Quarter 4	B50-22	8	6780	23.88	0.975	7.92	173.25	1017
CEA 1-36, Quarter 4	B50-23	9	6730	22.645	0.98	7.86	167	699.5
CEA 1-36, Quarter 4	B50-24	10	6885	23.1	0.985	7.965	175.1	496.55

Fe (mg/kg)	Mg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	P (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Sr (mg/kg)	V (mg/kg)	W (mg/kg)	Zn (mg/kg)
E 1946	202.8	11.48	717	3153	24.935	23.155	16.265	0.24	U 60.65	
E 1953	203.25	11.63	726	3093.5	25.51	23.47	16.47	0.22	U 60.2	

Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)	
E	2194		230		10.82		801.5		3170		23.64		19.05		16.19		0	U	76.7		
E	2261.5		234.75		10.84		627.5		3381.5		26.075		18.68		15.955		0.74	J	107.1		
E	2246		232.3		10.47		629		3550.5		28.78		18.095		15.18		0.32	U	68.8		
E	2195.5		228.5		10.905		627.5		3613.5		27.86		18.845		15.62		0.36	U	74.4		
E	2175.5		226.4		10.76		629.5		3010.5		21.765		19.15		15.74		0.31	U	76.1		
E	2160		224.65		10.585		625		3225.5		25.99		19.085		15.6		0.275	U	75.95		
E	2193		228.85		11.02		631.5		3207		24.27		19.445		15.76		0.24	U	72.35		
E	2115.4 45		220.7355		10.7969		636.805		3544.595		28.07295		19.7354		15.6651		0.2424	U	66.508 5		
E	2071.5		215		9.83		563		1197.5		8.365		20.205		15		0.165	U	57.9		
E	2055.5		210.6		10.6		576		1439.5		9.765		20.88		14.965		0.125	U	57.25		
E	2064		212.75		10.43		597		1582		10.895		20.455		14.95		0.17	U	61.1		
E	3492		351.2		12.11		674		1755.5		12.655		22.085		15.93		0.48	J	71.2		
E	2156		215.75		10.32		758.5		1472		11.55		18.075		14.4		-0.12	U	62.2		
E	2126		211.85		10.14		770		1399.5		9.33		19.365		14.535		-0.15	U	61.75		
E	2086.5		209.1		10.27		807		1291		8.595		20.19		14.575		-0.015	U	59.15		
E	2058		204.35		10.23		821		1346		8.92		21.095		14.765		-0.14	U	59.1		
E	2098.5		207.75		10.385		854.5		1382.5		8.49		20.68		14.515		-0.055	U	58.9		
E	2035.5		201.35		10.25		862.5		1599.5		11.025		20.805		14.065		-0.125	U	59.15		
E	2103.5		206.45		10.75		867.5		1219		7.89		21.295		14.05		-0.095	U	60.6		
D	2144.5		217.6		10.595		947		1215.5		8.38		21.635		15.08		-0.045	U	59.95		
D	2092.5		209.05		10.495		950		1368.5		9.24		21.775		14.725		-0.09	U	60.25		
D	2087		207.75		10.435		976		1347		9.34		22.8		15.095		-0.055	U	69.75		
D	2058.5		204.1		10.525		983		1267.5		8.695		22.885		15.1		-0.045	U	61.95		

Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)	
D	2071		205.45		10.6		994		1259.5		8.595		22.805		15.01		-0.07	U	63.6		
D	2077.5		205.4		10.645		1011.5		1235		8.795		22.975		15.005		-0.075	U	60.8		
D	2023		201.2		10.555		1028		1308		8.985		21.795		14.505		0	U	61.05		
D	2078.5		205.6		10.67		1052.5		1238.5		8.105		22.39		14.85		0.025	U	71.3		
D	2064		203.15		10.59		1073		1354.5		8.72		22.745		14.605		-0.08	U	56.65		
D	2010.7 75		199.41		10.76975		1192.55		2856.025		22.747		22.931		15.48475		-0.0345	U	78.43		
D	2063.5		205.3		10.755		1210		3257		27.28		23.795		15.78		-0.085	U	60.1		
D	2056.5		204.85		10.87		1215		3043		26.63		23.72		15.815		0.14	U	119.9		
D	2058		203.6		10.875		1228.5		3318.5		29.155		22.92		15.49		-0.025	U	61.05		
D	2064.5		204.55		10.68		1245.5		3185.5		24.535		21.955		14.64		-0.08	U	61.55		
D	2046		203.05		10.835		1263		3504.5		29.21		22.01		14.855		-0.085	U	67.95		
D	2070		203.3		10.88		1273.5		3059.5		25.535		22.53		15.055		-0.07	U	63.4		
D	2084.5		205.7		10.895		1277		3212.5		26.945		22.555		14.915		0.225	U	111.15		
D	2043		199.6		10.985		1305.5		2952		24.68		22.445		14.675		0.055	U	81.8		
D	2044.5		200.8		10.64		1320		2980		24.75		22.845		15.205		0.02	U	61.6		

Table A5. Experiment 5—Unground and puck mill metal results.

Exp ID	Lab Rep	Unground	Grinder Type	Ground Time (s)	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
B39-8	1	x	NA	0	3972	15.3	1.04	6.34	5.92	312
B39-9	2	x	NA	0	4020	15.7	1.07	6.38	5.88	357
B39-10	3	x	NA	0	4102	23.4	1.09	6.26	5.88	313
B39-11	4	x	NA	0	4078	16.4	1.07	6.42	6.16	676
B39-12	5	x	NA	0	4210	16.6	1.08	6.55	5.72	327
B39-13	6	x	NA	0	4214	16.5	1.09	6.62	6.74	329
B39-14	7	x	NA	0	4145	16.7	1.07	6.54	6.22	349
B39-15	8	x	NA	0	4079	16.0	1.07	6.36	6.16	351
B39-16	9	x	NA	0	3954	15.2	1.10	6.73	6.52	319
B39-17	10	x	NA	0	4118	16.4	1.09	6.51	5.93	322
B39-18	11	x	NA	0	4137	17.3	1.07	6.41	6.14	344
B39-19	12	x	NA	0	4218	22.8	1.08	6.56	5.99	323
B39-20	13	x	NA	0	4266	16.2	1.07	6.52	6.41	327
B39-21	14	x	NA	0	4118	15.8	1.08	6.35	5.88	360
B39-22	15	x	NA	0	4237	16.3	1.11	6.72	6.32	344
B39-26	1	NA	Puck	5x60	5490	32.0	1.85	8.77	233	503
B39-27	2	NA	Puck	5x60	5545	33.3	1.85	8.84	232	492
B39-28	3	NA	Puck	5x60	5585	32.1	1.86	8.94	229	391
B39-29	4	NA	Puck	5x60	5605	32.3	1.84	8.81	229	541
B39-30	5	NA	Puck	5x60	5505	31.7	1.80	8.82	225	417
B39-31	6	NA	Puck	5x60	5505	31.8	1.80	8.74	231	517
B39-32	7	NA	Puck	5x60	5425	31.3	1.80	8.79	230	574

Exp ID	Lab Rep	Unground	Grinder Type	Ground Time (s)	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
B39-33	8	NA	Puck	5x60	5450	31.5	1.80	8.72	232	473
B39-34	9	NA	Puck	5x60	5435	31.2	1.79	8.72	227	636
B39-35	10	NA	Puck	5x60	5485	31.5	1.84	8.84	223	425
B39-36	11	NA	Puck	5x60	5485	30.4	1.84	8.75	233	586
B39-37	12	NA	Puck	5x60	5475	30.3	1.83	8.67	236	570
B39-38	13	NA	Puck	5x60	5520	30.3	1.82	8.75	233	462
B39-39	14	NA	Puck	5x60	5505	29.4	1.82	8.64	222	458
B39-40	15	NA	Puck	5x60	5615	34.8	1.79	8.46	222	394

Fe (mg/kg)	Mg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	P (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Sr (mg/kg)	V (mg/kg)	W (mg/kg)	Zn (mg/kg)
9205	2004	199	8.91	570	1187	7.78	11.8	9.265	0.280	U 63.3
9340	1983	201	9.09	558	2194	23.0	12.2	9.38	0.295	U 65.5
9405	2041	206	8.93	557	3340	44.3	11.9	10.0	0.230	U 61.9
9255	2010	198	9.12	557	1129	8.12	11.9	9.82	0.395	U 107
9270	2005	201	9.08	553	1287	10.0	12.7	10.1	0.205	U 62.4
9428	1999	201	9.07	569	1890	12.5	12.7	10.8	0.247	U 62.3
9255	1991	197	8.97	548	1004	6.86	13.7	9.83	0.205	U 64.2
9325	2030	202	9.08	567	1505	13.7	12.9	9.88	0.210	U 64.1
9455	2041	200	9.65	562	1432	11.2	12.1	9.72	0.365	U 65.1
9400	2047	206	9.18	549	1183	7.82	12.1	9.96	0.265	U 63.7
9315	2055	200	9.07	563	1802	18.3	12.7	9.9	0.295	U 64.2

Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)
9353		2055		202		8.85		573		1440		10.9		12.9		10.5		0.393	U	60.7
9120		2010		200		9.14		552		1140		8.35		12.8		10.1		0.215	U	60.0
9150		1988		198		8.93		551		2307		22.6		13.1		9.99		0.240	U	65.0
9330		2008		199		9.25		566		1159		8.08		13.0		10.5		0.245	U	62.6
16565	D	2270		237		12.4		571		2779		21.8		20.6		15.3		0.540	J	83.7
16120	D	2284		240		12.4		578		2818		22.7		21.0		15.4		0.350	U	80.4
16955	D	2290		240		12.5		589		2776		22.2		20.9		15.6		0.320	U	72.2
16475	D	2286		240		12.4		581		2699		20.6		21.2		15.5		0.290	U	83.4
16095	D	2242		235		12.3		583		2859		22.9		20.6		15.3		0.275	U	74.5
16650	D	2257		235		12.4		584		2818		22.7		20.5		15.3		0.280	U	85.1
16995	D	2250		234		12.4		587		2657		20.9		20.3		15.1		0.310	U	92.9
17175	D	2256		236		12.6		591		2607		20.9		20.3		15.1		0.235	U	80.1
16150	D	2255		234		12.4		589		2779		22.3		20.1		15.0		0.245	U	90.5
17620	D	2265		238		12.5		600		2936		22.2		20.3		15.4		0.215	U	74.7
17165	D	2234		235		12.5		591		2690		21.0		20.5		15.1		0.370	U	85.2
17170	D	2220		234		12.5		600		2679		19.9		21.2		15.1		0.410	J	93.5
14775	D	2215		234		12.4		602		2866		22.6		20.6		15.2		0.275	U	78.5
16915	D	2176		229		12.3		610		2927		24.9		20.6		14.9		0.305	U	73.9
17320	D	2141		225		12.2		597		2509		18.9		21.0		14.7		0.210	U	67.0`

Table A6. Experiment 6—Results for comparison of different milling equipment.

Experiment ID	Grinder Type	Ground Time (s)	Lab	Al (mg/kg)	Ba (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
UN-0-2	Unground	0	TA	3560	11.60	NA	0.08	U 4.30	4.80	313
UN-0-4	Unground	0	TA	3560	12.10	NA	0.08	U 4.17	4.42	872
UN-0-6	Unground	0	TA	3590	11.90	NA	0.08	U 4.64	4.50	10900
UN-0-8	Unground	0	TA	3490	11.90	NA	0.08	U 4.33	4.27	299
UN-0-10	Unground	0	TA	3670	12.50	NA	0.08	U 4.32	4.71	339
UN-0-12	Unground	0	TA	3540	12.10	NA	0.08	U 4.10	4.55	323
UN-0-14	Unground	0	TA	3310	10.90	NA	0.08	U 4.20	4.24	301
UN-0-16	Unground	0	TA	3690	12.70	NA	0.08	U 4.86	4.62	368
UN-0-18	Unground	0	TA	3650	12.70	NA	0.08	U 4.33	4.45	309
UN-0-20	Unground	0	TA	3620	11.80	NA	0.08	U 4.43	4.55	336
UN-0-22	Unground	0	TA	3550	12.60	NA	0.08	U 4.22	4.36	301
UN-0-24	Unground	0	TA	3520	11.80	NA	0.08	U 4.55	4.72	333
UN-0-26	Unground	0	TA	3500	11.60	NA	0.08	U 4.42	4.34	314
UN-0-28	Unground	0	TA	3230	10.90	NA	0.08	U 4.17	3.91	306
UN-0-30	Unground	0	TA	3590	12.00	NA	0.08	U 4.44	4.58	299
AY27878	Puck	5x60	APPL	3251	17.09	NA	0.065	4.604	115.6	356.3
AY27879	Puck	5x60	APPL	3073	15.4	NA	0.048	4.411	116.4	281
AY27880	Puck	5x60	APPL	2905	14.59	NA	0.048	4.154	106.7	267.1
AY27881	Puck	5x60	APPL	2942	14.8	NA	0.056	4.335	107.8	278.1
AY27882	Puck	5x60	APPL	2836	13.68	NA	0.048	4.067	106.4	265.3
AY27883	Puck	5x60	APPL	2948	14.95	NA	0.047	4.277	108.4	256.2
AY27884	Puck	5x60	APPL	3079	14.94	NA	0.053	4.455	112.3	287.6

Experiment ID	Grinder Type	Ground Time (s)	Lab	Al (mg/kg)	Ba (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
AY27885	Puck	5x60	APPL	2918	14.74	NA	0.049	4.21	106.9	324.9
AY27886	Puck	5x60	APPL	2797	14.62	NA	0.046	4.108	102.4	282
AY27887	Puck	5x60	APPL	2944	14.39	NA	0.051	4.211	107.6	285.7
AY27888	Puck	5x60	APPL	2897	14.28	NA	0.053	4.225	107.1	261.6
AY27889	Puck	5x60	APPL	2942	13.82	NA	0.045	4.228	102.8	271.2
AY27890	Puck	5x60	APPL	2756	13.71	NA	0.048	4.15	102.4	259.4
AY27891	Puck	5x60	APPL	2934	14.34	NA	0.046	4.361	108.1	263.9
AY27892	Puck	5x60	APPL	2727	13.33	NA	0.048	3.91	103.5	242.2
B49-6	MP	5x60	CRREL	4128	18.655	NA	0.495	6.375	6.43	324.95
B49-7	MP	5x60	CRREL	3752.5	17.125	NA	0.37	5.855	6.065	278.15
B49-8	MP	5x60	CRREL	4054.5	17.2	NA	0.415	6.5	6.23	327.15
B49-9	MP	5x60	CRREL	3985.5	18.065	NA	0.41	6.5	6.245	353.25
B49-10	MP	5x60	CRREL	4041	17.64	NA	0.41	6.14	6.27	352.25
B49-11	MP	5x60	CRREL	4110.5	17.955	NA	0.43	6.495	6.515	355.75
B49-12	MP	5x60	CRREL	4034	17.885	NA	0.4	6.14	6.37	328.55
B49-13	MP	5x60	CRREL	4044	17.505	NA	0.405	6.29	6.45	319.55
B49-14	MP	5x60	CRREL	4246.5	18.01	NA	0.445	6.475	6.38	885.5
B49-15	MP	5x60	CRREL	4234	17.32	NA	0.42	6.405	6.225	319.7
B49-16	MP	5x60	CRREL	4047.5	15.37	NA	0.39	5.965	5.625	309.4
B49-17	MP	5x60	CRREL	4358	16.185	NA	0.42	6.115	6.06	319.95
B49-18	MP	5x60	CRREL	4500.5	17.36	NA	0.415	6.725	6.065	387.45
B49-19	MP	5x60	CRREL	4467	16.49	NA	0.415	6.355	6.445	371
B49-20	MP	5x60	CRREL	4598.5	16.885	NA	0.43	6.37	6.525	346.5

Experiment ID	Grinder Type	Ground Time (s)	Lab	Al (mg/kg)	Ba (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
B39-8	Unground	NA	CRREL	3971.5	15.325	NA	1.035	6.34	5.92	312.1
B39-9	Unground	NA	CRREL	4019.5	15.675	NA	1.065	6.375	5.88	357.25
B39-10	Unground	NA	CRREL	4101.5	23.385	NA	1.085	6.255	5.875	312.55
B39-11	Unground	NA	CRREL	4078	16.37	NA	1.065	6.42	6.16	675.5
B39-12	Unground	NA	CRREL	4210	16.585	NA	1.075	6.545	5.72	327.05
B39-13	Unground	NA	CRREL	4214.2	16.458	NA	1.0908	6.6155	6.7418	328.96
B39-14	Unground	NA	CRREL	4145	16.715	NA	1.07	6.535	6.22	349.1
B39-15	Unground	NA	CRREL	4079	16.035	NA	1.065	6.36	6.155	351.25
B39-16	Unground	NA	CRREL	3954	15.205	NA	1.1	6.725	6.52	319.4
B39-17	Unground	NA	CRREL	4117.5	16.36	NA	1.09	6.51	5.925	322.1
B39-18	Unground	NA	CRREL	4137	17.315	NA	1.065	6.41	6.14	343.9
B39-19	Unground	NA	CRREL	4218.2	22.7511	NA	1.0812	6.5586	5.9925	323.44
B39-20	Unground	NA	CRREL	4265.5	16.23	NA	1.065	6.515	6.405	326.85
B39-21	Unground	NA	CRREL	4117.5	15.835	NA	1.08	6.345	5.88	360
B39-22	Unground	NA	CRREL	4236.5	16.28	NA	1.105	6.715	6.32	343.75
B39-26	Puck	5x60	CRREL	5490	32.02	NA	1.845	8.765	232.9	503
B39-27	Puck	5x60	CRREL	5545	33.3	NA	1.85	8.84	232.45	492
B39-28	Puck	5x60	CRREL	5585	32.12	NA	1.86	8.935	229	391.25
B39-29	Puck	5x60	CRREL	5605	32.305	NA	1.835	8.81	228.75	540.5
B39-30	Puck	5x60	CRREL	5505	31.695	NA	1.8	8.82	224.8	416.75
B39-31	Puck	5x60	CRREL	5505	31.835	NA	1.8	8.74	231.05	517
B39-32	Puck	5x60	CRREL	5425	31.32	NA	1.795	8.79	229.95	573.5
B39-33	Puck	5x60	CRREL	5450	31.465	NA	1.8	8.715	231.65	472.5

Experiment ID	Grinder Type	Ground Time (s)	Lab	Al (mg/kg)		Ba (mg/kg)		Ca (mg/kg)		Cd (mg/kg)		Co (mg/kg)		Cr (mg/kg)		Cu (mg/kg)	
B39-34	Puck	5x60	CRREL	5435		31.165		NA		1.785		8.72		227.45		635.5	
B39-35	Puck	5x60	CRREL	5485		31.485		NA		1.835		8.835		223.2		424.9	
B39-36	Puck	5x60	CRREL	5485		30.395		NA		1.835		8.75		233.3		585.5	
B39-37	Puck	5x60	CRREL	5475		30.325		NA		1.83		8.67		236.25		570	
B39-38	Puck	5x60	CRREL	5520		30.275		NA		1.815		8.75		232.65		461.5	
B39-39	Puck	5x60	CRREL	5505		29.42		NA		1.815		8.635		221.6		457.85	
B39-40	Puck	5x60	CRREL	5615		34.8		NA		1.785		8.455		221.65		394.25	
B40-8	Puck	5x60	CRREL	5840		30.46		NA		1.8		8.66		218.85		601	
B40-9	Puck	5x60	CRREL	5770		30.3		NA		1.8		8.575		220.85		544.5	
B40-10	Puck	5x60	CRREL	5740		29.53		NA		1.77		8.405		218.4		485.75	
B40-11	Puck	5x60	CRREL	5850		29.465		NA		1.805		8.455		218.55		564	
B40-12	Puck	5x60	CRREL	6010		29.305		NA		1.825		8.48		217.15		540	
B40-13	Puck	5x60	CRREL	6045		29.125		NA		1.8		8.365		216.4		802	
B40-14	Puck	5x60	CRREL	6065		28.62		NA		1.82		8.36		216.55		703.5	
B40-15	Puck	5x60	CRREL	6235		28.82		NA		1.865		8.565		218.4		813	
B40-16	Puck	5x60	CRREL	6205		28.41		NA		1.83		8.39		218		517.5	
B40-17	Puck	5x60	CRREL	6195		27.45		NA		1.86		8.38		215.95		551.5	
B40-18	Puck	5x60	CRREL	6185		27.59		NA		1.835		8.325		216.1		636	
B40-19	Puck	5x60	CRREL	6250		27.135		NA		1.87		8.365		214.75		572	
B40-20	Puck	5x60	CRREL	6195		28.16		NA		1.825		8.295		213.9		535	
B40-21	Puck	5x60	CRREL	6455		26.025		NA		1.895		8.325		213.95		592.5	
B40-22	Puck	5x60	CRREL	6800		25.92		NA		1.945		8.315		216.1		611.5	
CEA37-LP3-6	Puck & Ring	5x60	TA	5760		40.9		3100		<2.00		6.88		355		333	

Experiment ID	Grinder Type	Ground Time (s)	Lab	Al (mg/kg)	Ba (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
CEA37-LP3-7	Puck & Ring	5x60	TA	5870	42	3150	<2.00	7.05	362	367
CEA37-LP3-8	Puck & Ring	5x60	TA	5970	42.5	3240	<2.00	7.16	367	347
CEA37-LP3-9	Puck & Ring	5x60	TA	5690	40.5	3100	<2.00	6.89	352	340
CEA37-LP3-10	Puck & Ring	5x60	TA	5630	39.9	3170	<2.00	6.93	357	357
CEA37-LP3-11	Puck & Ring	5x60	TA	6020	42.9	3250	<2.00	7.17	362	362
CEA37-LP3-12	Puck & Ring	5x60	TA	6150	43.6	3350	<2.00	7.46	379	368
CEA37-LP3-13	Puck & Ring	5x60	TA	5120	36.4	2810	<2.00	6.3	317	308
CEA37-LP3-14	Puck & Ring	5x60	TA	5360	38.1	2990	<2.00	6.67	338	332
CEA37-LP3-15	Puck & Ring	5x60	TA	5500	39.1	3050	<2.00	6.68	344	341
S5-01	Ball Mill	18 hrs	TA	4980	31.8	2710	<2.00	5.96	9.38	316
S5-02	Ball Mill	18 hrs	TA	5040	32.7	2730	<2.00	6.04	9.51	315
S5-03	Ball Mill	18 hrs	TA	5030	31.9	2710	<2.00	5.95	9.4	317
S5-04	Ball Mill	18 hrs	TA	4960	31.8	2690	<2.00	5.94	9.38	318
S5-05	Ball Mill	18 hrs	TA	4990	31.8	2690	<2.00	5.95	9.34	318
S5-06	Ball Mill	18 hrs	TA	5060	32.4	2750	<2.00	5.98	9.42	349
S5-07	Ball Mill	18 hrs	TA	5000	32	2710	<2.00	6.02	9.36	313
S5-08	Ball Mill	18 hrs	TA	5030	32.1	2730	<2.00	5.98	9.38	325
S5-09	Ball Mill	18 hrs	TA	5020	31.5	2710	<2.00	6.08	9.54	320
S5-10	Ball Mill	18 hrs	TA	5000	32.2	2700	<2.00	6	9.34	314
S5-11	Ball Mill	18 hrs	TA	4950	31.8	2680	<2.00	5.98	9.25	320
S5-12	Ball Mill	18 hrs	TA	4920	31.6	2730	<2.00	5.96	9.28	313
S5-13	Ball Mill	18 hrs	TA	4970	31.8	2720	<2.00	6.1	9.4	314
S5-14	Ball Mill	18 hrs	TA	4960	31.9	2720	<2.00	6.07	9.38	328

Experiment ID	Grinder Type	Ground Time (s)	Lab	Al (mg/kg)	Ba (mg/kg)	Ca (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
S5-15	Ball Mill	18 hrs	TA	4840	31.1	2660	<2.00	5.93	9.19	309

Fe (mg/kg)	Mg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	P (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Sr (mg/kg)	K (mg/kg)	Na (mg/kg)	S (mg/kg)	V (mg/kg)	W (mg/kg)	Zn (mg/kg)
9260	NA	178	7.20 J	NA	2280	16.90	NA	NA	NA	NA	6.39	NA	48.20
9210	NA	182	7.20 J	NA	1340	7.12	NA	NA	NA	NA	6.32	NA	49.00
9310	NA	180	9.15	NA	1060	4.42	NA	NA	NA	NA	5.91	NA	574.00
9070	NA	172	7.10 J	NA	1800	11.50	NA	NA	NA	NA	6.14	NA	46.80
9470	NA	183	7.50 J	NA	1600	7.74	NA	NA	NA	NA	6.50	NA	49.70
9100	NA	179	7.20 J	NA	1170	5.38	NA	NA	NA	NA	6.32	NA	48.90
8670	NA	169	7.00 J	NA	1330	7.37	NA	NA	NA	NA	5.92	NA	46.60
9730	NA	185	7.80	NA	1920	14.00	NA	NA	NA	NA	6.58	NA	52.70
9290	NA	182	7.40 J	NA	4760	60.90	NA	NA	NA	NA	6.15	NA	49.50
9350	NA	183	7.60	NA	1970	10.30	NA	NA	NA	NA	6.30	NA	50.50
9120	NA	180	7.20 J	NA	1030	5.18	NA	NA	NA	NA	6.40	NA	47.90
9200	NA	182	7.50 J	NA	2130	11.00	NA	NA	NA	NA	6.13	NA	48.50
9170	NA	179	7.40 J	NA	1570	7.23	NA	NA	NA	NA	6.09	NA	48.70
8320	NA	161	6.90 J	NA	5190	60.20	NA	NA	NA	NA	5.49	NA	46.20
9330	NA	194	7.55	NA	1490	9.64	NA	NA	NA	NA	6.20	NA	48.20
8325	1668	155.2	6.984	364.9	2500	8.908	9.597	NA	NA	NA	6.135	NA	54.17
8086	1578	145.3	6.735	348.1	2540	7.931	9.294	NA	NA	NA	6.124	NA	48.35
7665	1526	141.3	6.375	330.8	3780	13.99	8.85	NA	NA	NA	5.645	NA	49.07

Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		K (mg/kg)		Na (mg/kg)		S (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)	
7717		1498		141.8		6.424		335.1		3840		15.9		8.612		NA		NA		NA		5.702		NA		50.1	
7477		1468		139.2		6.251		328.2		3110		10.47		8.463		NA		NA		NA		5.385		NA		48.6	
7788		1541		142.6		6.489		329.7		2800		10.34		9.044		NA		NA		NA		5.987		NA		49.88	
7973		1598		148.9		6.759		346.1		2930		11.7		9.201		NA		NA		NA		5.947		NA		52.63	
7762		1503		141.6		6.385		342.8		3830		15.49		8.764		NA		NA		NA		5.783		NA		55.27	
7411		1462		136.5		6.254		326.3		2990		10.34		8.443		NA		NA		NA		5.6		NA		49.79	
7614		1516		142.1		6.377		330.7		2800		10.87		8.847		NA		NA		NA		5.754		NA		51.47	
7693		1518		141.5		6.365		329.9		2660		9.201		8.738		NA		NA		NA		5.646		NA		49.17	
7554		1502		142.8		6.486		331.5		3060		11.97		8.652		NA		NA		NA		5.67		NA		48.08	
7406		1448		136		6.289		321.6		2680		9.227		8.375		NA		NA		NA		5.48		NA		48.85	
7739		1503		142.8		6.61		337.1		3030		10.92		8.68		NA		NA		NA		5.788		NA		48.08	
7317		1470		134.5		6.103		318.8		3060		10.28		8.38		NA		NA		NA		5.166		NA		45.73	
14025	D	2118		193.8		8.41		586.5		2241		18.565		12.62		NA				NA		10.73		0.285	U	69.65	
12665	D	1993		175.2		7.845		521.5		973		6.36		10.73		NA		NA		NA		9.46		0.195	U	61.95	
13900	D	2139		190.25		8.455		598		1163.5		7.08		12.215		NA		NA		NA		10.12		0.195	U	68.2	
13850	D	2058		187.1		8.23		565.5		1259		7.82		12.93		NA		NA		NA		10.405		0.225	U	69.9	
13280	D	2078		185.3		8.26		550		1071.5		7.095		12.8		NA		NA		NA		10.115		0.235	U	72.65	
14295	D	2109.5		188.85		8.655		598		1025		7.185		13.635		NA		NA		NA		10.6		0.49	J	73.9	
14105	D	2064.5		186.15		8.09		593.5		2370.5		26.74		12.91		NA		NA		NA		10.58		0.31	U	67.25	
13575	D	2032		184.85		8.035		596.5		1155.5		7.65		13.475		NA		NA		NA		10.43		0.305	U	67	
14470	D	2068		188		8.45		644		1750		12.79		14.08		NA		NA		NA		10.64		0.765	J	141.95	
13335	D	2023.5		184.1		8.285		608.5		1425.5		9.92		13.93		NA		NA		NA		10.315		0.235	U	65	
12905	D	1939.5		176.75		8.245		605		1559.5		15.775		12.965		NA		NA		NA		9.185		0.195	U	62.4	

Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		K (mg/kg)		Na (mg/kg)		S (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)	
14125	D	1946.5		177.2		8.655		596.5		1026		6.815		13.85		NA		NA		NA		9.965		0.215	U	63.25	
14335	D	1924		183.35		8.41		639		1117		7.83		15.16		NA		NA		NA		10.475		0.215	U	64.2	
14390	D	1921		176.75		8.72		608.5		1155		8.28		14.86		NA		NA		NA		10.675		0.155	U	64.6	
14010	D	1957		183.2		8.75		627		1095		7.94		16.935		NA		NA		NA		10.68		0.205	U	61.2	
9205		2004		199.1		8.91		570		1187		7.78		11.815		NA		NA		NA		9.265		0.28	U	63.3	
9340		1983		200.65		9.09		557.5		2193.5		23.045		12.23		NA		NA		NA		9.38		0.295	U	65.5	
9405		2040.5		206.05		8.925		556.5		3340		44.265		11.87		NA		NA		NA		10.005		0.23	U	61.9	
9255		2010		198.45		9.12		556.5		1128.5		8.12		11.945		NA		NA		NA		9.815		0.395	U	106.55	
9270		2004.5		201.3		9.08		553		1287		10.01		12.65		NA		NA		NA		10.135		0.205	U	62.35	
9428.4		1998.8		200.94		9.0698		568.63		1889.7		12.509		12.721		NA		NA		NA		10.817		0.2475	U	62.267	
9255		1991		196.65		8.97		548		1003.5		6.86		13.73		NA		NA		NA		9.825		0.205	U	64.2	
9325		2030		201.55		9.08		566.5		1504.5		13.74		12.91		NA		NA		NA		9.88		0.21	U	64.05	
9455		2040.5		200.45		9.65		562		1432		11.215		12.07		NA		NA		NA		9.72		0.365	U	65.05	
9400		2046.5		205.5		9.18		548.5		1182.5		7.82		12.055		NA		NA		NA		9.955		0.265	U	63.7	
9315		2055		199.9		9.065		562.5		1801.5		18.345		12.65		NA		NA		NA		9.9		0.295	U	64.2	
9353.4		2054.8		201.5		8.8485		573.24		1439.7		10.858		12.929		NA		NA		NA		10.521		0.3927	U	60.741	
9120		2009.5		200.35		9.14		552		1140		8.345		12.755		NA		NA		NA		10.13		0.215	U	60	
9150		1988		197.5		8.925		551		2306.5		22.56		13.075		NA		NA		NA		9.99		0.24	U	64.95	
9330		2007.5		198.95		9.25		565.5		1159		8.075		12.985		NA		NA		NA		10.515		0.245	U	62.55	
16565	D	2269.5		237.45		12.405		570.5		2779		21.8		20.635		NA		NA		NA		15.255		0.54	J	83.7	
16120	D	2283.5		239.65		12.425		578		2818		22.675		20.98		NA		NA		NA		15.42		0.35	U	80.35	
16955	D	2289.5		239.8		12.475		588.5		2775.5		22.2		20.885		NA		NA		NA		15.595		0.32	U	72.15	
16475	D	2286		239.85		12.41		580.5		2699		20.55		21.15		NA		NA		NA		15.495		0.29	U	83.35	

Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		K (mg/kg)		Na (mg/kg)		S (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)	
16095	D	2242		234.9		12.32		583		2859		22.885		20.625		NA		NA		NA		15.315		0.275	U	74.45	
16650	D	2256.5		235.15		12.395		584		2818		22.72		20.535		NA		NA		NA		15.285		0.28	U	85.1	
16995	D	2249.5		234.2		12.43		587		2657		20.905		20.33		NA		NA		NA		15.08		0.31	U	92.85	
17175	D	2255.5		235.75		12.57		590.5		2606.5		20.855		20.305		NA		NA		NA		15.12		0.235	U	80.1	
16150	D	2255		234.35		12.415		589		2779		22.32		20.1		NA		NA		NA		14.995		0.245	U	90.45	
17620	D	2265		237.6		12.49		599.5		2936		22.2		20.305		NA		NA		NA		15.385		0.215	U	74.7	
17165	D	2233.5		234.5		12.48		591		2689.5		21.025		20.505		NA		NA		NA		15.07		0.37	U	85.2	
17170	D	2219.5		234.4		12.52		600		2678.5		19.89		21.17		NA		NA		NA		15.085		0.41	J	93.5	
14775	D	2214.5		233.5		12.42		602		2865.5		22.61		20.605		NA		NA		NA		15.16		0.275	U	78.5	
16915	D	2176		229		12.325		610		2927		24.92		20.59		NA		NA		NA		14.925		0.305	U	73.85	
17320	D	2141		224.9		12.155		597		2509		18.905		20.96		NA		NA		NA		14.73		0.21	U	67	
16565	D	2080.5		221.6		11.95		614.5		2487.5		20.345		22.325		NA		NA		NA		15.54		0.285	U	76.5	
16230	D	2100		222.85		11.995		621		2648.5		22.48		21.855		NA		NA		NA		15.275		0.265	U	83.2	
17135	D	2064		220.3		11.88		614.5		2738		22.415		22.015		NA		NA		NA		15.065		0.24	U	70.6	
16925	D	2061.5		220.6		11.89		618.5		2788		23.785		22.285		NA		NA		NA		15.375		0.5	J	75.5	
16505	D	2009		217.2		11.835		623.5		2439.5		21.58		23.175		NA		NA		NA		15.47		0.3	U	69.2	
16505	D	2017		215.1		11.81		621.5		2706.5		24.045		22.975		NA		NA		NA		15.045		0.295	U	82.65	
16725	D	1995.5		214.1		11.89		623.5		2674		23.9		23.41		NA		NA		NA		15.09		0.27	U	76.1	
15530	D	2009		216.5		12.08		631.5		2779		23.655		23.735		NA		NA		NA		15.36		0.31	U	92.65	
17170	D	1987		213.4		11.815		634		2751		24.44		23.745		NA		NA		NA		15.315		0.235	U	65.65	
17505	D	1970.5		211.65		12.71		643.5		2546		22.615		23.96		NA		NA		NA		14.995		0.215	U	67.55	
17080	D	1994		212.75		11.94		637.5		2682		23.81		23.7		NA		NA		NA		14.955		0.16	U	70.55	
17715	D	1966		210.8		11.99		646		2705.5		23.83		23.91		NA		NA		NA		14.99		0.23	U	72.55	

Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		K (mg/kg)		Na (mg/kg)		S (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)	
16605	D	2029		217.9		11.755		634.5		2752.5		23.955		23.59		NA		NA		NA		14.725		0.195	U	65.3	
17285	D	1925.5		206.25		11.855		650		2729.5		24.19		24.715		NA		NA		NA		14.99		0.395	U	67.15	
16940	D	1904.5		205		11.815		655		2671.5		25.545		26.25		NA		NA		NA		15.3		0.3	U	64.65	
14100		2130		219		13.2		382		2330		5.26		NA		1600		663		23.4		14.3		NA		49.1	
14400		2190		226		13.5		393		2410		5.4		NA		1650		676		22.7		14.7		NA		53	
14600		2240		229		13.7		401		2430		4.51		NA		1670		678		22.2		14.7		NA		54.9	
14100		2120		218		13.1		383		2340		5.18		NA		1590		648		21.8		14.3		NA		49.8	
14000		2160		223		13.2		383		2350		4.91		NA		1600		640		22.3		14.5		NA		50.2	
14900		2220		228		13.6		400		2400		5.14		NA		1660		685		22.3		14.8		NA		52.2	
15300		2320		238		14.2		413		2550		5.53		NA		1720		692		22.8		15.4		NA		53.4	
13200		1930		199		12		345		2110		5.93		NA		1420		579		18.6		13.1		NA		45	
13700		2050		212		12.8		369		2260		5.33		NA		1510		601		19.5		13.8		NA		47.2	
13700		2080		214		12.8		371		2310		4.77		NA		1530		615		20.1		13.7		NA		50	
17200		2220		226		9.42		409		1690		3.46		NA		1230		332		19.1		10.7		NA		52.2	
17400		2220		227		9.44		425		1700		4.02		NA		1250		337		19.1		11		NA		52.1	
17300		2210		224		9.39		420		1700		3.54		NA		1210		330		18.4		10.7		NA		52	
17100		2180		223		9.31		422		1680		3.85		NA		1210		327		17.6		10.8		NA		51	
17100		2220		227		9.32		427		1670		3.34		NA		1230		334		18.5		10.6		NA		51.4	
17500		2260		229		9.41		430		1690		3.71		NA		1250		338		19		10.8		NA		53.8	
17300		2200		225		9.43		434		1680		3.54		NA		1220		331		17.8		10.8		NA		51	
17200		2210		226		9.44		437		1710		3.43		NA		1220		330		18		10.7		NA		53.7	
17400		2270		232		9.53		438		1710		3.69		NA		1220		345		17.7		11		NA		52.8	
17200		2200		225		9.4		428		1700		3.18		NA		1220		329		15.2		10.8		NA		50.9	

Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		K (mg/kg)		Na (mg/kg)		S (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)	
17100		2210		227		9.3		428		1680		3.47		NA		1230		329		15.3		10.7		NA		50.9	
17100		2200		225		9.23		426		1680		3.19		NA		1230		328		13.9		10.9		NA		51.6	
17400		2230		229		9.46		433		1690		3.37		NA		1240		329		14.2		11		NA		50.1	
17300		2190		226		9.41		429		1680		3.17		NA		1220		326		14.5		11		NA		51.2	
17000		2160		223		9.22		423		1640		3.14		NA		1200		318		14.1		10.6		NA		49.9	

Table A7. Experiment 7—Results comparing different milling intervals for the puck mill and ball mill (concentrations in mg/kg).

Exp ID	Lab Rep	Grinder Type	Ground Time (s)	Al	Ba	Cd	Co	Cr	Cu	
B47-29	1	Puck	30	4345	21.4	0.785	6.93	71.5	321	
B47-30	2	Puck	30	4416	21.3	0.780	6.98	79.9	315	
B47-31	3	Puck	30	4296	21.3	0.770	7.44	74.6	302	
B47-32	4	Puck	30	4399	20.5	0.800	6.75	78.6	330	
B47-33	5	Puck	30	4435	20.2	0.790	6.77	77.9	328	
B47-34	6	Puck	30	4497	19.9	0.765	6.66	72.8	340	
B47-35	7	Puck	30	4680	19.9	0.785	6.90	77.2	367	
B47-36	8	Puck	30	5135	20.8	0.870	6.80	84.1	406	
B47-37	9	Puck	30	4777	19.2	0.785	6.47	73.9	350	
B47-38	10	Puck	30	4893	18.6	0.790	6.25	69.4	360	
B47-39	11	Puck	30	5225	19.4	0.855	6.70	73.7	385	
B47-40	12	Puck	30	5290	18.6	0.855	6.64	70.8	395	
B47-41	13	Puck	30	5100	19.1	0.865	6.77	78.6	401	
B47-42	14	Puck	30	4841	17.1	0.830	6.44	68.7	349	
B47-43	15	Puck	30	4981	17.0	0.865	6.22	69.6	411	
B48-7	1	Puck	60	5630	29.7	0.965	8.17	137	408	
B48-8	2	Puck	60	5420	27.5	0.955	7.80	133	604	
B48-9	3	Puck	60	5425	28.0	0.930	8.03	131	474	
B48-10	4	Puck	60	5860	29.6	0.970	8.15	139	421	
B48-11	5	Puck	60	5590	29.6	0.960	8.05	137	504	
B48-12	6	Puck	60	5070	30.6	0.904	7.97	132	521	

Exp ID	Lab Rep	Grinder Type	Ground Time (s)	Al	Ba	Cd	Co	Cr	Cu	
B48-13	7	Puck	60	5295	30.2	0.915	8.09	136	362	
B48-14	8	Puck	60	5165	29.3	0.905	7.87	132	366	
B48-15	9	Puck	60	5255	29.2	0.925	8.20	138	376	
B48-16	10	Puck	60	4886	27.3	0.885	7.73	131	350	
B48-17	11	Puck	60	5305	29.2	0.935	8.09	136	363	
B48-18	12	Puck	60	5355	29.6	0.915	8.09	134	355	
B48-19	13	Puck	60	5475	30.4	0.925	8.30	139	380	
B48-20	14	Puck	60	5545	29.9	0.920	8.11	138	577	
B48-21	15	Puck	60	5390	28.9	0.910	8.01	135	388	
B48-24	1	Puck	90	5360	25.0	0.955	7.49	156	493	
B48-25	2	Puck	90	6105	27.3	1.00	7.72	159	444	
B48-26	3	Puck	90	6145	26.0	1.01	7.59	157	426	
B48-27	4	Puck	90	7205	28.4	1.16	8.34	180	487	
B48-28	5	Puck	90	6790	25.0	1.06	7.68	162	508	
B48-29	6	Puck	90	6865	24.1	1.07	7.63	157	1123	
B48-30	7	Puck	90	7070	26.0	1.10	8.01	173	610	
B48-31	8	Puck	90	6845	24.2	1.07	7.60	160	553	
B48-32	9	Puck	90	6195	25.0	1.07	7.99	168	938	
B48-33	10	Puck	90	6340	24.1	1.04	7.62	165	817	
B48-34	11	Puck	90	6620	23.6	1.05	7.69	167	616	
B48-35	12	Puck	90	6515	22.8	1.03	7.45	152	750	
B48-36	13	Puck	90	6435	24.2	1.04	7.59	163	578	
B48-37	14	Puck	90	6715	23.2	1.05	7.63	161	512	

Exp ID	Lab Rep	Grinder Type	Ground Time (s)	Al	Ba	Cd	Co	Cr	Cu	
B48-38	15	Puck	90	6570	22.0	1.05	7.41	155	835	
B48-41	1	Puck	120	7350	23.3	1.13	7.86	230	557	
B48-42	2	Puck	120	8240	23.9	1.21	8.17	238	644	
B48-43	3	Puck	120	7660	23.6	1.15	8.05	233	628	
B48-44	4	Puck	120	7705	24.5	1.17	8.05	234	559	
B48-45	5	Puck	120	7700	23.9	1.20	8.13	235	771	
B48-46	6	Puck	120	7605	24.3	1.18	8.12	235	589	
B48-47	7	Puck	120	7695	24.0	1.16	8.06	235	564	
B48-48	8	Puck	120	7790	23.5	1.18	8.04	229	666	
B49-21	9	Puck	120	5875	33.2	0.56	8.09	234	417	
B49-22	10	Puck	120	6440	32.2	0.57	8.36	249	399	
B49-23	11	Puck	120	6205	30.0	0.55	7.83	231	404	
B49-24	12	Puck	120	6295	28.6	0.58	7.79	227	451	
B49-25	13	Puck	120	6755	28.5	0.57	7.84	226	441	
B49-26	14	Puck	120	7000	29.0	0.58	7.93	231	511	
B49-27	15	Puck	120	7020	29.1	0.58	7.92	233	475	
B39-26	1	Puck	5x60	5490	32.0	1.85	8.77	233	503	
B39-27	2	Puck	5x60	5545	33.3	1.85	8.84	232	492	
B39-28	3	Puck	5x60	5585	32.1	1.86	8.94	229	391	
B39-29	4	Puck	5x60	5605	32.3	1.84	8.81	229	541	
B39-30	5	Puck	5x60	5505	31.7	1.80	8.82	225	417	
B39-31	6	Puck	5x60	5505	31.8	1.80	8.74	231	517	
B39-32	7	Puck	5x60	5425	31.3	1.80	8.79	230	574	

Exp ID	Lab Rep	Grinder Type	Ground Time (s)	Al	Ba	Cd	Co	Cr	Cu	
B39-33	8	Puck	5x60	5450	31.5	1.80	8.72	232	473	
B39-34	9	Puck	5x60	5435	31.2	1.79	8.72	227	636	
B39-35	10	Puck	5x60	5485	31.5	1.84	8.84	223	425	
B39-36	11	Puck	5x60	5485	30.4	1.84	8.75	233	586	
B39-37	12	Puck	5x60	5475	30.3	1.83	8.67	236	570	
B39-38	13	Puck	5x60	5520	30.3	1.82	8.75	233	462	
B39-39	14	Puck	5x60	5505	29.4	1.82	8.64	222	458	
B39-40	15	Puck	5x60	5615	34.8	1.79	8.46	222	394	
BM-8-2	1	Ball Mill	28800	4170	19.60	0.08	U 4.56	6.33	898	
BM-8-4	2	Ball Mill	28800	4190	19.30	0.08	U 4.78	6.35	999	
BM-8-6	3	Ball Mill	28800	4290	20.10	0.08	U 4.75	6.50	947	
BM-8-8	4	Ball Mill	28800	4380	20.40	0.08	U 4.85	6.61	1030	
BM-8-10	5	Ball Mill	28800	4350	20.50	0.08	U 4.89	6.62	1060	
BM-8-12	6	Ball Mill	28800	4330	20.30	0.08	U 4.80	6.48	1040	
BM-8-14	7	Ball Mill	28800	4300	20.30	0.08	U 4.78	6.42	997	
BM-8-16	8	Ball Mill	28800	4220	20.20	0.08	U 4.72	6.67	1140	
BM-8-18	9	Ball Mill	28800	4250	19.80	0.08	U 4.60	6.40	1030	
BM-8-20	10	Ball Mill	28800	4190	20.00	0.08	U 4.71	6.25	964	
BM-8-22	11	Ball Mill	28800	4250	20.10	0.08	U 4.71	6.48	1010	
BM-8-24	12	Ball Mill	28800	4320	20.20	0.08	U 4.77	6.53	1040	
BM-8-26	13	Ball Mill	28800	4310	20.80	0.08	U 4.75	6.42	1030	
BM-8-28	14	Ball Mill	28800	4240	19.90	0.08	U 4.62	6.38	963	
BM-8-30	15	Ball Mill	28800	4340	20.50	0.08	U 4.78	6.59	1050	

Exp ID	Lab Rep	Grinder Type	Ground Time (s)	Al	Ba	Cd	Co	Cr	Cu	
BM-12-2	1	Ball Mill	43200	4580	22.30	0.08	U 4.87	7.69	1030	
BM-12-4	2	Ball Mill	43200	4430	21.60	0.08	U 4.69	7.54	1030	
BM-12-6	3	Ball Mill	43200	4690	22.90	0.08	U 4.96	7.82	1080	
BM-12-8	4	Ball Mill	43200	4660	22.60	0.08	U 5.04	7.73	1060	
BM-12-10	5	Ball Mill	43200	4590	22.80	0.08	U 4.99	7.68	1070	
BM-12-12	6	Ball Mill	43200	4720	23.20	0.08	U 5.17	7.88	1060	
BM-12-14	7	Ball Mill	43200	4650	22.70	0.08	U 5.02	8.14	1020	
BM-12-16	8	Ball Mill	43200	4610	22.40	0.08	U 4.91	7.66	1010	
BM-12-18	9	Ball Mill	43200	4700	23.20	0.08	U 4.88	7.78	1060	
BM-12-20	10	Ball Mill	43200	4670	22.90	0.08	U 5.01	7.87	1080	
BM-12-22	11	Ball Mill	43200	4660	22.60	0.08	U 4.97	7.78	1080	
BM-12-24	12	Ball Mill	43200	4610	22.30	0.08	U 5.06	7.72	1050	
BM-12-26	13	Ball Mill	43200	4590	22.30	0.08	U 4.90	7.72	988	
BM-12-28	14	Ball Mill	43200	3980	19.40	0.08	U 4.50	6.52	939	
BM-12-30	15	Ball Mill	43200	4680	22.90	0.08	U 4.89	7.74	1030	
BM-16-2	1	Ball Mill	57600	4730	26.00	0.08	U 4.77	9.15	1240	
BM-16-4	2	Ball Mill	57600	4900	27.20	0.08	U 4.91	9.44	1200	
BM-16-6	3	Ball Mill	57600	4820	26.80	0.08	U 4.72	9.26	1120	
BM-16-8	4	Ball Mill	57600	4830	26.60	0.08	J 4.79	9.47	1200	
BM-16-10	5	Ball Mill	57600	4860	26.90	0.08	J 4.77	9.43	1220	
BM-16-12	6	Ball Mill	57600	4730	25.90	0.07	J 4.78	9.22	1200	
BM-16-14	7	Ball Mill	57600	4810	26.30	0.08	U 4.79	9.42	1150	
BM-16-16	8	Ball Mill	57600	4830	26.70	0.08	U 4.77	9.47	1180	

Exp ID	Lab Rep	Grinder Type	Ground Time (s)	Al	Ba	Cd	Co	Cr	Cu	
BM-16-18	9	Ball Mill	57600	4820	26.70	0.08	U 4.87	9.41	1200	
BM-16-20	10	Ball Mill	57600	4650	25.80	0.08	U 4.80	9.23	1200	
BM-16-22	11	Ball Mill	57600	4810	26.60	0.08	U 4.87	9.42	1180	
BM-16-24	12	Ball Mill	57600	4790	26.90	0.08	U 4.83	9.27	1150	
BM-16-26	13	Ball Mill	57600	4710	25.90	0.08	U 4.79	9.40	1220	
BM-16-28	14	Ball Mill	57600	4510	25.10	0.08	U 4.65	8.91	1120	
BM-16-30	15	Ball Mill	57600	4620	25.90	0.08	U 4.82	9.29	1160	
BM-20-2	1	Ball Mill	72000	5060	29.10	0.08	U 4.84	10.50	1330	
BM-20-4	2	Ball Mill	72000	5030	29.10	0.08	U 4.88	10.40	1340	
BM-20-6	3	Ball Mill	72000	5100	29.50	0.08	U 4.88	10.50	1330	
BM-20-8	4	Ball Mill	72000	4990	28.70	0.08	U 4.77	10.20	1300	
BM-20-10	5	Ball Mill	72000	5000	29.10	0.08	U 4.76	10.20	1330	
BM-20-12	6	Ball Mill	72000	5180	29.50	0.08	U 4.84	10.40	1340	
BM-20-14	7	Ball Mill	72000	5270	30.50	0.08	U 4.97	10.70	1330	
BM-20-16	8	Ball Mill	72000	5040	29.30	0.08	U 4.83	10.40	1330	
BM-20-18	9	Ball Mill	72000	4990	28.70	0.08	U 4.74	10.20	1260	
BM-20-20	10	Ball Mill	72000	5070	29.20	0.08	U 4.85	10.40	1300	
BM-20-22	11	Ball Mill	72000	5010	29.00	0.08	U 4.84	10.30	1330	
BM-20-24	12	Ball Mill	72000	5100	29.60	0.08	U 4.91	10.50	1320	
BM-20-26	13	Ball Mill	72000	5050	28.90	0.08	U 4.82	10.40	1280	
BM-20-28	14	Ball Mill	72000	5020	29.00	0.08	U 4.84	10.40	1300	
BM-20-30	15	Ball Mill	72000	4960	28.70	0.08	U 4.83	10.50	1310	

Fe		Mg		Mn		Ni		P		Pb		Sb		Sr		V		W		Zn	
14675	D	2005		192		8.72		724		2596		24.9		16.5		12.3		0.480	J	64.4	
14820	D	1989		192		9.17		712		3113		29.9		17.1		12.2		0.485	J	62.4	
13205	D	1973		188		8.66		727		2274		17.6		16.6		11.8		0.700	J	61.8	
14335	D	2021		197		8.95		737		1439		9.84		16.2		11.8		0.595	J	64.6	
14275	D	1840		182		8.86		716		2005		19.0		18.4		12.1		0.540	J	60.0	
14790	D	1829		184		8.83		715		2452		25.5		17.2		11.8		0.500	J	58.2	
14470	D	1822		181		8.87		711		1872		18.0		18.1		11.9		0.490	J	59.6	
15125	D	1913		192		9.70		791		4381		53.3		20.3		12.6		0.545	J	61.5	
13720	D	1754		175		8.77		698		1528		12.8		18.2		11.9		0.455	J	55.4	
13215	D	1729		173		8.92		709		3031		40.0		19.2		11.7		0.425	J	52.0	
14815	D	1799		180		9.38		764		1821		20.4		20.4		12.3		0.420	J	55.5	
15125	D	1744		177		9.46		747		1761		12.6		20.4		12.2		0.480	J	53.7	
14945	D	1893		188		9.99		825		1726		14.8		19.3		12.2		0.625	J	60.1	
14100	D	1741		176		9.09		754		1724		15.0		18.7		11.5		0.480	J	53.9	
13545	D	1673		170		9.04		763		3504		48.8		19.5		11.3		0.505	J	55.6	
15540	D	2232		231		10.6		586		1961		15.3		21.5		14.6		1.62	J	71.0	
15415	D	2195		226		10.4		591		2543		21.2		20.8		13.5		1.86	J	80.8	
15370	D	2120		220		10.3		569		2711		24.5		21.3		13.8		1.74	J	72.5	
15160	D	2176		227		10.6		597		2494		24.3		23.2		14.7		1.60	J	70.0	
15220	D	2207		228		10.4		583		2003		15.8		21.7		14.5		1.78	J	70.9	
15316	D	2215		224		9.74		552		2138		18.6		17.5		13.9		0.970	J	95.9	
15620	D	2230		226		10.1		575		1746		13.5		17.6		14.2		0.610	J	72.2	
15410	D	2159		221		9.70		557		2121		18.0		17.0		14.0		0.535	J	71.1	

Fe		Mg	Mn	Ni	P	Pb	Sb	Sr	V	W	Zn	
16335	D	2220	225	10.2	585	2233	20.2	17.0	14.1	0.535	J	73.2
14720	D	2149	216	10.2	560	1934	15.3	15.8	13.1	0.490	J	70.9
15685	D	2181	224	10.4	571	2156	16.7	17.2	14.1	0.510	J	70.7
16270	D	2170	222	9.93	571	2287	20.1	17.2	14.2	0.515	J	70.0
15800	D	2243	228	10.6	588	1980	14.7	17.8	14.6	0.515	J	72.5
16120	D	2175	225	10.1	581	2330	22.0	17.3	14.6	0.765	J	95.6
15970	D	2139	219	10.3	574	2176	19.0	16.9	14.2	0.460	J	70.2
16315	D	1989	207	10.2	565	2566	22.0	14.5	13.5	0.510	J	68.9
16900	D	1958	210	10.6	562	2515	22.1	15.5	15.2	0.425	J	60.8
16485	D	1885	203	10.7	547	2988	26.8	14.7	14.9	0.415	J	57.4
18515	D	2039	224	11.7	624	2474	20.9	16.0	16.7	0.500	J	62.5
16210	D	1836	200	11.1	574	3491	34.3	14.0	15.6	0.380	U	56.7
16885	D	1786	193	10.7	559	2917	27.0	13.2	15.4	0.830	J	99.1
16920	D	1906	208	11.4	609	2435	21.9	14.6	16.1	0.485	J	63.9
17700	D	1825	196	11.0	580	2898	27.7	13.5	15.2	0.390	U	58.3
18170	D	1944	205	11.8	608	2991	25.2	24.3	14.8	0.170	U	86.1
17545	D	1752	189	10.9	564	2569	19.3	25.7	14.9	0.075	U	68.3
15980	D	1716	185	11.3	548	2826	24.6	26.8	14.8	0.090	U	60.2
17125	D	1664	178	10.8	540	2985	24.7	26.4	14.5	0.115	U	63.5
17170	D	1745	188	11.1	561	2702	22.2	26.2	15.0	0.120	U	63.9
16185	D	1685	183	11.1	558	2744	23.9	27.3	14.9	0.065	U	54.0
15885	D	1632	177	11.2	562	3176	29.3	26.6	14.3	0.110	U	76.7
16710	D	1669	184	12.6	586	2295	19.2	29.6	14.5	0.155	U	54.5

Fe		Mg	Mn	Ni	P	Pb	Sb	Sr	V	W	Zn	
18745	D	1703	187	13.1	609	2391	20.6	33.2	15.6	0.225	U	57.0
18425	D	1693	186	12.8	596	2581	21.8	31.0	14.9	0.120	U	55.0
18950	D	1714	189	12.9	589	2832	25.7	31.3	15.3	0.155	U	53.9
18785	D	1683	187	12.8	593	3071	28.6	31.1	15.4	0.155	U	68.3
17960	D	1727	190	13.1	600	3104	27.8	30.6	15.2	0.080	U	56.1
18215	D	1709	188	12.9	595	2748	24.7	31.2	15.3	0.050	U	54.8
17928	D	1681	185	12.8	594	2535	23.1	31.4	15.1	0.165	U	58.3
17995	D	2278	230	11.6	651	2482	18.5	20.3	16.2	0.510	J	71.9
18650	D	2183	225	12.2	693	1956	14.5	22.5	16.9	0.405	J	68.8
17315	D	2080	215	11.9	655	2509	19.4	21.6	15.9	0.290	U	63.1
17720	D	2033	209	11.9	668	2558	20.5	21.7	15.2	0.275	U	65.1
10770	E	1975	206	12.0	660	2732	22.6	23.6	15.9	0.285	U	60.9
10750	E	1988	209	12.4	673	2478	19.5	24.8	16.4	0.285	U	62.3
10870	E	1977	209	12.3	676	2162	17.0	24.9	16.6	0.255	U	62.1
16565	D	2270	237	12.4	571	2779	21.8	20.6	15.3	0.540	J	83.7
16120	D	2284	240	12.4	578	2818	22.7	21.0	15.4	0.350	U	80.4
16955	D	2290	240	12.5	589	2776	22.2	20.9	15.6	0.320	U	72.2
16475	D	2286	240	12.4	581	2699	20.6	21.2	15.5	0.290	U	83.4
16095	D	2242	235	12.3	583	2859	22.9	20.6	15.3	0.275	U	74.5
16650	D	2257	235	12.4	584	2818	22.7	20.5	15.3	0.280	U	85.1
16995	D	2250	234	12.4	587	2657	20.9	20.3	15.1	0.310	U	92.9
17175	D	2256	236	12.6	591	2607	20.9	20.3	15.1	0.235	U	80.1
16150	D	2255	234	12.4	589	2779	22.3	20.1	15.0	0.245	U	90.5

Fe		Mg	Mn	Ni	P	Pb	Sb	Sr	V	W	Zn	
17620	D	2265	238	12.5	600	2936	22.2	20.3	15.4	0.215	U	74.7
17165	D	2234	235	12.5	591	2690	21.0	20.5	15.1	0.370	U	85.2
17170	D	2220	234	12.5	600	2679	19.9	21.2	15.1	0.410	J	93.5
14775	D	2215	234	12.4	602	2866	22.6	20.6	15.2	0.275	U	78.5
16915	D	2176	229	12.3	610	2927	24.9	20.6	14.9	0.305	U	73.9
17320	D	2141	225	12.2	597	2509	18.9	21.0	14.7	0.210	U	67.0
11400		NA	196	7.98	NA	4630	33.10	NA	7.37	NA		66.30
11400		NA	195	8.05	NA	4410	29.80	NA	7.25	NA		69.20
11500		NA	197	8.11	NA	4520	33.50	NA	7.56	NA		66.60
11800		NA	203	8.28	NA	4990	34.20	NA	7.78	NA		69.70
11700		NA	201	8.38	NA	4530	31.90	NA	7.77	NA		71.60
11700		NA	199	8.17	NA	4680	32.00	NA	7.70	NA		66.90
11500		NA	200	8.05	NA	4590	32.00	NA	7.61	NA		67.90
11400		NA	198	8.31	NA	4650	32.50	NA	7.50	NA		76.40
11600		NA	199	8.08	NA	4630	32.20	NA	7.62	NA		66.70
11200		NA	197	8.03	NA	4910	34.50	NA	7.16	NA		70.20
11600		NA	196	8.03	NA	4850	36.50	NA	7.52	NA		68.40
11700		NA	201	8.28	NA	4580	33.30	NA	7.78	NA		70.00
11700		NA	200	8.20	NA	4740	33.90	NA	7.66	NA		69.50
11400		NA	197	8.06	NA	6420	59.10	NA	7.34	NA		69.30
11700		NA	202	8.31	NA	4670	34.30	NA	7.70	NA		69.20
13300		NA	193	8.75	NA	5670	43.60	NA	8.59	NA		78.90
12900		NA	187	8.42	NA	5470	41.70	NA	8.44	NA		76.20

Fe	Mg	Mn	Ni	P	Pb	Sb	Sr	V	W	Zn	
13700	NA	197	8.90	NA	5750	45.40	NA	9.00	NA	81.70	
13500	NA	197	8.85	NA	5900	45.70	NA	8.91	NA	81.00	
13300	NA	195	8.76	NA	5500	43.90	NA	8.74	NA	80.50	
13700	NA	200	8.99	NA	6030	47.30	NA	8.92	NA	82.70	
13500	NA	197	9.02	NA	6090	48.40	NA	8.77	NA	81.00	
13400	NA	194	8.74	NA	5790	46.00	NA	8.77	NA	78.70	
13700	NA	198	8.90	NA	6240	55.00	NA	8.98	NA	82.00	
13500	NA	198	8.95	NA	6010	48.20	NA	8.88	NA	81.40	
13500	NA	197	8.90	NA	5770	44.10	NA	8.70	NA	81.10	
13400	NA	195	8.89	NA	5610	42.50	NA	8.61	NA	82.10	
13300	NA	194	8.79	NA	5650	43.80	NA	8.62	NA	80.40	
11700	NA	169	8.04	NA	—	E —	NA	6.90	NA	71.70	
13600	NA	196	8.78	NA	5720	47.00	NA	8.78	NA	81.20	
13800	NA	199	8.48	NA	6450	47.80	NA	7.42	NA	90.60	
14100	NA	205	8.67	NA	6550	46.10	NA	7.69	NA	92.00	
13900	NA	199	8.46	NA	6250	46.40	NA	7.67	NA	89.00	
14000	NA	203	8.77	NA	6430	45.50	NA	7.88	NA	91.10	
14000	NA	202	8.72	NA	6420	46.60	NA	7.72	NA	91.20	
13800	NA	201	8.55	NA	6320	43.80	NA	7.66	NA	89.90	
14000	NA	204	8.65	NA	6360	43.10	NA	7.82	NA	91.60	
14000	NA	206	8.74	NA	6450	54.10	NA	8.03	NA	92.50	
14000	NA	205	8.76	NA	6450	42.20	NA	7.81	NA	92.80	
13700	NA	202	8.66	NA	6300	42.10	NA	7.73	NA	90.60	

Fe		Mg		Mn		Ni		P		Pb		Sb		Sr		V		W		Zn	
14000		NA		204		8.77		NA		6310		42.40		NA		7.91		NA		90.50	
13800		NA		203		8.61		NA		6440		44.00		NA		7.72		NA		90.00	
13800		NA		202		8.63		NA		6300		42.80		NA		7.75		NA		98.20	
13200		NA		196		8.37		NA		6240		44.70		NA		7.55		NA		87.90	
13600		NA		204		8.68		NA		6430		45.30		NA		7.91		NA		92.10	
—	E	NA		210		—	E	NA		7150		56.10		NA		8.59		NA		93.60	
—	E	NA		211		—	E	NA		7180		56.70		NA		8.51		NA		93.10	
—	E	NA		212		—	E	NA		7340		57.50		NA		8.52		NA		93.90	
—	E	NA		206		—	E	NA		7060		53.30		NA		8.36		NA		92.30	
—	E	NA		206		—	E	NA		7070		55.70		NA		8.38		NA		92.00	
—	E	NA		209		—	E	NA		7160		54.40		NA		8.52		NA		91.90	
—	E	NA		214		—	E	NA		7280		54.90		NA		8.77		NA		92.40	
—	E	NA		209		—	E	NA		7120		55.40		NA		8.59		NA		93.30	
—	E	NA		205		—	E	NA		7030		54.10		NA		8.34		NA		91.90	
—	E	NA		209		—	E	NA		7180		54.40		NA		8.25		NA		94.00	
—	E	NA		208		—	E	NA				54.20		NA		8.35		NA		93.70	
—	E	NA		211		—	E	NA				56.10		NA		8.50		NA		96.70	
—	E	NA		208		—	E	NA				54.30		NA		8.50		NA		93.60	
—	E	NA		210		—	E	NA				55.00		NA		8.60		NA		94.10	
—	E	NA		208		—	E	NA				56.10		NA		8.39		NA		94.30	

Table A8. Experiment 8—Results by digestion mass.

Sample ID	Lab Rep	Digestion Mass (g)	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	
B40-8	16	2.00	5840	30.46	1.8	8.66	218.85	601	
B40-9	17	2.00	5770	30.3	1.8	8.575	220.85	544.5	
B40-10	18	2.00	5740	29.53	1.77	8.405	218.4	485.75	
B40-11	19	2.00	5850	29.465	1.805	8.455	218.55	564	
B40-12	20	2.00	6010	29.305	1.825	8.48	217.15	540	
B40-13	21	2.00	6045	29.125	1.8	8.365	216.4	802	
B40-14	22	2.00	6065	28.62	1.82	8.36	216.55	703.5	
B40-15	23	2.00	6235	28.82	1.865	8.565	218.4	813	
B40-16	24	2.00	6205	28.41	1.83	8.39	218	517.5	
B40-17	25	2.00	6195	27.45	1.86	8.38	215.95	551.5	
B40-18	26	2.00	6185	27.59	1.835	8.325	216.1	636	
B40-19	27	2.00	6250	27.135	1.87	8.365	214.75	572	
B40-20	28	2.00	6195	28.16	1.825	8.295	213.9	535	
B40-21	29	2.00	6455	26.025	1.895	8.325	213.95	592.5	
B40-22	30	2.00	6800	25.92	1.945	8.315	216.1	611.5	
B41-6	1	1.00	5305	28.595	0.61	7.62	222.05	511	
B41-7	2	1.00	5085	26.56	0.565	7.58	222.2	415.45	
B41-8	3	1.00	5475	28.845	0.58	7.74	223.15	889	
B41-9	4	1.00	5385	28.7	0.57	7.515	221.35	511	
B41-10	5	1.00	5720	29.965	0.595	7.98	228.8	657	
B41-11	6	1.00	5610	29.76	0.565	7.785	226.1	576	

Sample ID	Lab Rep	Digestion Mass (g)	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
B41-12	7	1.00	5675	30.055	0.6	8.015	229.05	531
B41-13	8	1.00	5445	29.365	0.58	7.815	222.35	501.5
B41-14	9	1.00	5275	26.805	0.55	7.545	223.3	485.7
B41-15	10	1.00	5355	26.455	0.565	7.675	224.95	579
B41-16	11	1.00	5740	29.105	0.58	7.79	227.45	431.45
B41-17	12	1.00	5745	29	0.575	7.86	226.5	1140
B41-18	13	1.00	5916	29.0292	0.5712	7.7826	230.418	443.241
B41-19	14	1.00	5805	28.05	0.61	7.735	223.7	998.5
B41-20	15	1.00	5720	28.08	0.575	7.675	224.8	478.75
0.5-R1	1	0.50	5119	30.06	0.97	8.48	221.3	382.4
0.5-R2	2	0.50	5199	29.98	0.97	8.61	221.6	423.8
0.5-R3	3	0.50	5096	29.35	0.98	8.43	218.6	474.9
0.5-R4	4	0.50	5363.16	30.9876	0.9894	8.8842	228.174	595.272
0.5-R5	5	0.50	5276	30.39	0.97	8.62	224.9	370.4
0.5-R6	6	0.50	5255	29.52	0.99	8.77	228.7	634.9
0.5-R7	7	0.50	5383.04	30.7528	0.9672	8.9648	228.384	401.336
0.5-R8	8	0.50	5049	28.02	0.96	8.32	214.5	446.5
0.5-R9	9	0.50	4961	28.58	0.95	8.33	215.6	509.4
0.5-R10	10	0.50	4859	27.03	0.94	8.32	214.3	372.7
0.5-R11	11	0.50	4827	25.73	0.96	8.65	209.9	636.8
0.5-R12	12	0.50	5099	27.44	0.98	8.59	213.9	529.3
0.5-R13	13	0.50	5117	27.24	0.96	8.33	214.2	390.4

Sample ID	Lab Rep	Digestion Mass (g)	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	
0.5-R14	14	0.50	5078	27.17	0.94	8.42	213.8	380	
0.5-R15	15	0.50	5061	26.69	0.93	8.53	210.7	443.3	
B42-4	1	5.00	5430	27.335	1.135	8.515	227.1	479.35	
B42-5	2	5.00	5510	27.035	1.125	8.595	226	915.5	
B42-6	3	5.00	5625	27.95	1.115	8.6	231.5	554.5	
B42-7	4	5.00	5530	27.56	1.15	8.635	227.7	603	
B42-8	5	5.00	5155	33.405	0.515	7.81	223.95	589	
B42-9	6	5.00	5095	28.84	0.5	7.83	222.85	450.9	
B42-10	7	5.00	5205	28.525	0.505	7.815	223.15	444.3	
B42-11	8	5.00	5230	28.265	0.495	7.8	221.9	535	
B42-12	9	5.00	5275	29.495	0.51	7.815	221.85	494.6	
B42-13	10	5.00	5280	27.69	0.5	7.72	219.3	485.25	
B42-14	11	5.00	5285	27.405	0.505	7.755	220.05	434.35	
B42-15	12	5.00	5375	27.685	0.51	7.655	217.8	477.8	
B42-16	13	5.00	5265	27.605	0.49	7.765	217.95	461.75	
B42-17	14	5.00	5315	27.655	0.485	7.795	219.75	496.65	
B42-18	15	5.00	5090	27.31	0.495	7.66	215.6	466.5	
B42-21	1	10.00	5325	28.745	0.495	7.54	217	531.5	
B42-22	2	10.00	5265	28.42	0.475	7.505	216.2	479.5	
B42-23	3	10.00	5400	28.585	0.47	7.53	217.3	539	
B42-24	4	10.00	5484.3	28.58805	0.4949	7.56995	217.857	482.881	
B42-25	5	10.00	5410	28.29	0.47	7.46	215.2	600.5	

Sample ID	Lab Rep	Digestion Mass (g)	Al (mg/kg)	Ba (mg/kg)	Cd (mg/kg)	Co (mg/kg)	Cr (mg/kg)	Cu (mg/kg)
B42-26	6	10.00	5410	28.67	0.485	7.505	214.95	530.5
B42-27	7	10.00	5560	27.94	0.495	7.505	217	685
B42-28	8	10.00	5325	28.135	0.485	7.415	216.85	550.5
B42-29	9	10.00	5245	26.79	0.465	7.27	209	518.5
B42-30	10	10.00	5565	26.905	0.495	7.405	214.65	546.5
B42-31	11	10.00	5780	26.445	0.485	7.345	213.25	686
B42-32	12	10.00	5825	26.375	0.48	7.29	211.15	518.5
B42-33	13	10.00	5755	25.89	0.49	7.275	209.2	537.5
B42-34	14	10.00	5815	26.11	0.495	7.26	211.15	599
B42-35	15	10.00	5900	25.395	0.485	7.235	210.1	514

Fe (mg/kg)	Mg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	P (mg/kg)	Pb (mg/kg)	Sb (mg/kg)	Sr (mg/kg)	V (mg/kg)	W (mg/kg)	Zn (mg/kg)
16565	D 2080.5	221.6	11.95	614.5	2487.5	20.345	22.325	15.54	0.285	U 76.5
16230	D 2100	222.85	11.995	621	2648.5	22.48	21.855	15.275	0.265	U 83.2
17135	D 2064	220.3	11.88	614.5	2738	22.415	22.015	15.065	0.24	U 70.6
16925	D 2061.5	220.6	11.89	618.5	2788	23.785	22.285	15.375	0.5	J 75.5
16505	D 2009	217.2	11.835	623.5	2439.5	21.58	23.175	15.47	0.3	U 69.2
16505	D 2017	215.1	11.81	621.5	2706.5	24.045	22.975	15.045	0.295	U 82.65
16725	D 1995.5	214.1	11.89	623.5	2674	23.9	23.41	15.09	0.27	U 76.1
15530	D 2009	216.5	12.08	631.5	2779	23.655	23.735	15.36	0.31	U 92.65
17170	D 1987	213.4	11.815	634	2751	24.44	23.745	15.315	0.235	U 65.65

Fe (mg/kg)		Mg (mg/kg)		Mn (mg/kg)		Ni (mg/kg)		P (mg/kg)		Pb (mg/kg)		Sb (mg/kg)		Sr (mg/kg)		V (mg/kg)		W (mg/kg)		Zn (mg/kg)	
17505	D	1970.5		211.65		12.71		643.5		2546		22.615		23.96		14.995		0.215	U	67.55	
17080	D	1994		212.75		11.94		637.5		2682		23.81		23.7		14.955		0.16	U	70.55	
17715	D	1966		210.8		11.99		646		2705.5		23.83		23.91		14.99		0.23	U	72.55	
16605	D	2029		217.9		11.755		634.5		2752.5		23.955		23.59		14.725		0.195	U	65.3	
17285	D	1925.5		206.25		11.855		650		2729.5		24.19		24.715		14.99		0.395	U	67.15	
16940	D	1904.5		205		11.815		655		2671.5		25.545		26.25		15.3		0.3	U	64.65	
16730	D	2194		228.15		11.945		858.5		3030.5		25.145		19.81		14.03		0.235	U	79.2	
16575	D	2172		225.8		11.945		871.5		2746.5		22.08		19.135		13.635		0.21	U	73.6	
17465	D	2175		226.1		11.835		862		2641.5		20.36		20.66		14.605		0.205	U	101.05	
16415	D	2103		222.5		11.495		853.5		2544.5		18.875		20.84		14.61		0.195	U	75.85	
16040	D	2202.5		231.6		12.145		895.5		2921.5		23.105		22.005		15.34		0.17	U	87.4	
16085	D	2212		231.4		11.885		897.5		3180		28.31		21.42		14.785		0.205	U	90.1	
17680	D	2203.5		230.3		11.955		914		2692.5		19.605		21.68		15.32		0.425	J	79.1	
16370	D	2179		225.7		11.88		907.5		2936		22.555		20.475		14.47		0.29	U	79.55	
16795	D	2129		224.6		11.83		949		3045.5		23.78		20.29		13.775		0.29	U	76.4	
17340	D	2200.5		229.05		12.24		998		3201.5		26.43		20.175		13.685		0.245	U	83.85	
16860	D	2172.5		228.5		12.01		967.5		3055		23.93		21.9		14.795		0.495	U	71.85	
16670	D	2136.5		225.05		12.09		946.5		2747		21.775		22.055		15.06		0.19	U	111.75	
17498.1	D	2127.21		227.664		11.9289		973.59		2879.46		22.6083		23.154		15.0246		0.1836	U	70.38	
17490	D	2104.5		222.25		11.805		965.5		3149.5		27.53		22.175		14.69		0.24	U	100.6	
16745	D	2091		223		11.71		968		2923		23.81		22.32		14.645		0.18	U	71.05	
14690	D	2158		231.5		11.61		688		2727		23.55		19.49		14.12		0.51	U	73.49	

Fe (mg/kg)		Mg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	P (mg/kg)		Pb (mg/kg)	Sb (mg/kg)	Sr (mg/kg)	V (mg/kg)		W (mg/kg)	Zn (mg/kg)
16590	D	2149	231.3	11.36	693		2516	21.89	19.68	14.49		0.47	U 73.35
16320	D	2103	227.1	11.21	690.4		2896	23.5	19.67	14.03		0.47	U 77.73
15167.4	D	2194.02	238.068	11.7606	713.286		2748.9	23.5314	20.5734	14.9532		0.4692	U 85.2822
16270	D	2157	233.1	11.32	693.1		2886	24.15	20.13	14.57		0.37	U 71.83
16150	D	2136	230.6	11.06	734.4		3229	29.67	19.95	14.72		0.53	U 99.7
14799.2	D	2213.12	238.68	11.5648	735.8		3077.36	27.508	20.1968	14.6432		0.2808	U 75.7744
15530	D	2115	227.6	11.45	712.4		3017	26.07	18.77	13.24		0.36	U 82.89
15560	D	2123	227.7	10.91	699.6		2694	21.6	18.7	13.59		0.7	U 80.33
15910	D	2088	224.9	11.18	731.9		2610	21.19	18.42	13.2		0.43	U 71.58
16300	D	2071	228.6	10.48	766		2815	25.7	18.15	13.78		0.45	U 89.52
15450	D	2097	230	10.69	770.3		2924	25.34	19.17	13.41		0.32	U 81.59
14000	D	2066	223.8	10.85	743.1		3287	30.55	19.94	13.58		0.28	U 72.38
15470	D	2047	221.4	11.28	746.8		2816	23.46	18.94	13.52		0.32	U 70.85
16230	D	2087	224.2	11.03	755.7		2483	21.85	18.47	13.39		0.32	U 79.02
17150	D	2099	230.3	12.885	734		3079	25.94	20.935	14.3		0.66	J 78.55
15485	D	2060	227.65	12.955	740		2993	24.255	21.075	14.42		0.965	J 122.05
17195	D	2077	231.1	12.945	740.5		2937.5	23.645	21.85	14.705		0.635	J 79.95
15930	D	2089	232.55	13.07	749.5		3065	25.07	21.31	14.345		0.655	J 83.45
17040	D	2352	243.8	12.28	579		2659	19.575	19.775	15.06		0.455	J 89.15
16205	D	2225.5	231.65	12.21	586.5		2823	21.235	19.555	15.015		0.31	U 80.85
17185	D	2203.5	229.9	12.18	586		2777.5	21.06	20.105	15.055		0.22	U 76.1
17230	D	2167	226.2	12.295	586.5		2843.5	21.495	20.275	15.055		0.22	U 81.45

Fe (mg/kg)		Mg (mg/kg)	Mn (mg/kg)	Ni (mg/kg)	P (mg/kg)		Pb (mg/kg)	Sb (mg/kg)	Sr (mg/kg)	V (mg/kg)		W (mg/kg)	Zn (mg/kg)
16870	D	2145.5	224.2	12.1	586		2753	19.78	20.44	15.08		0.145	U 77.35
16515	D	2124.5	222.8	12.075	584		2705	20.375	20.74	15.06		0.235	U 79.55
17285	D	2118.5	221.85	12.165	591		2775.5	21.815	20.515	14.775		0.07	U 71.55
16875	D	2097.5	221.95	11.91	582.5		2734.5	21.41	20.975	14.98		0.11	U 73.9
15860	D	2103.5	221.2	12.005	583		2648.5	19.515	20.64	14.925		0.08	U 72.85
17195	D	2114	222.15	12.105	592.5		2683	19.76	20.73	14.93		0.1	U 76.1
16885	D	2125	221.35	11.935	582		2751	21.13	19.775	14.6		0.235	U 75.5
16605	D	2101	217	11.735	572.5		2560	15.45	20.945	14.715		0.215	U 77.75
16000	D	2103.5	218	11.71	571		2668	16.63	20.75	14.685		0.185	U 79.2
15455	D	2084	217.4	11.735	577.5		2595.5	15.915	21.38	14.85		0.145	U 77.8
17028.6	D	2078.58	217.0995	11.7665	579.235		2693.67	16.766	21.816	14.88235		0.06565	U 73.4775
16455	D	2059	214.85	11.6	572		2642	16.975	21.55	14.645		0.15	U 80.7
17315	D	2053.5	214.95	11.605	573		2619	16.23	21.385	14.75		0.055	U 74.95
16830	D	2034.5	213.35	11.65	582		2573.5	17.675	22.12	14.935		0.155	U 83.05
16500	D	2075	213.05	11.655	586		2719.5	16.065	20.95	14.21		0.34	U 79.95
16390	D	2025.5	210	11.465	574.5		2553.5	15.55	20.6	13.865		0.18	U 73.6
16805	D	1996.5	209.5	11.625	590.5		2697.5	18.275	22.1	14.41		0.15	U 73.7
15920	D	1931	204.2	11.495	583.5		2646	16.78	23.075	14.545		0.17	U 80.3
16240	D	1918.5	203.5	11.3	580.5		2597.5	17.345	23.37	14.37		0.075	U 69.35
16765	D	1934.5	205.35	11.44	587.5		2592	17.515	22.79	14.035		0.07	U 69.05
16375	D	1921	202.75	11.36	587.5		2555	16.91	23.125	14.31		0.11	U 70.85
16700	D	1895.5	199.75	11.395	597.5		2611	16.775	23.435	14.01		-0.005	U 66.1

Table A9. Experiment 9—Results by digestion interval; concentrations in mg/kg.

Exp ID	Lab Rep	Digestion Time (hrs)	Al	Ba	Cd	Co	Cr	Cu
B40-8	16	12	5840	30.46	1.8	8.66	218.85	601
B40-9	17	12	5770	30.3	1.8	8.575	220.85	544.5
B40-10	18	12	5740	29.53	1.77	8.405	218.4	485.75
B40-11	19	12	5850	29.465	1.805	8.455	218.55	564
B40-12	20	12	6010	29.305	1.825	8.48	217.15	540
B40-13	21	12	6045	29.125	1.8	8.365	216.4	802
B40-14	22	12	6065	28.62	1.82	8.36	216.55	703.5
B40-15	23	12	6235	28.82	1.865	8.565	218.4	813
B40-16	24	12	6205	28.41	1.83	8.39	218	517.5
B40-17	25	12	6195	27.45	1.86	8.38	215.95	551.5
B40-18	26	12	6185	27.59	1.835	8.325	216.1	636
B40-19	27	12	6250	27.135	1.87	8.365	214.75	572
B40-20	28	12	6195	28.16	1.825	8.295	213.9	535
B40-21	29	12	6455	26.025	1.895	8.325	213.95	592.5
B40-22	30	12	6800	25.92	1.945	8.315	216.1	611.5
B44-6	1	24	6215	33.35	1.005	9.045	244.2	618.5
B44-7	2	24	6130	32.69	0.985	8.94	242.4	573
B44-8	3	24	6060	32.32	0.98	8.855	243.7	419.95
B44-9	4	24	6155	32.635	1	8.94	239.25	661
B44-10	5	24	6130	32.725	0.96	8.93	241.1	394.2
B44-11	6	24	6181	33.673	1.081	9.065	247.55	520.15
B44-12	7	24	6055	33.275	1.055	8.995	245.1	421.95

Exp ID	Lab Rep	Digestion Time (hrs)	Al		Ba		Cd		Co		Cr		Cu	
B44-13	8	24	6070		31.865		1.09		9.015		246.55		507	
B44-14	9	24	4479		24.25		0.835		7.175		202.8		288.3	
B44-16	11	24	5855		29.855		1.065		8.96		241.7		556	
B44-17	12	24	6115		30.785		1.065		8.865		242.55		489.35	
B44-18	13	24	5870		29.08		1.055		8.77		237.1		416.9	
B44-19	14	24	6080		30.07		1.075		8.75		241.7		462.9	
B44-20	15	24	6005		29.64		1.045		8.71		240.2		725.5	

Fe		Mg		Mn		Ni		P		Pb		Sb		Sr		V		W		Zn	
16565	D	2080.5		221.6		11.95		614.5		2487.5		20.345		22.325		15.54		0.285	U	76.5	
16230	D	2100		222.85		11.995		621		2648.5		22.48		21.855		15.275		0.265	U	83.2	
17135	D	2064		220.3		11.88		614.5		2738		22.415		22.015		15.065		0.24	U	70.6	
16925	D	2061.5		220.6		11.89		618.5		2788		23.785		22.285		15.375		0.5	J	75.5	
16505	D	2009		217.2		11.835		623.5		2439.5		21.58		23.175		15.47		0.3	U	69.2	
16505	D	2017		215.1		11.81		621.5		2706.5		24.045		22.975		15.045		0.295	U	82.65	
16725	D	1995.5		214.1		11.89		623.5		2674		23.9		23.41		15.09		0.27	U	76.1	
15530	D	2009		216.5		12.08		631.5		2779		23.655		23.735		15.36		0.31	U	92.65	
17170	D	1987		213.4		11.815		634		2751		24.44		23.745		15.315		0.235	U	65.65	
17505	D	1970.5		211.65		12.71		643.5		2546		22.615		23.96		14.995		0.215	U	67.55	
17080	D	1994		212.75		11.94		637.5		2682		23.81		23.7		14.955		0.16	U	70.55	
17715	D	1966		210.8		11.99		646		2705.5		23.83		23.91		14.99		0.23	U	72.55	
16605	D	2029		217.9		11.755		634.5		2752.5		23.955		23.59		14.725		0.195	U	65.3	

Fe		Mg		Mn		Ni		P		Pb		Sb		Sr		V		W		Zn	
17285	D	1925.5		206.25		11.855		650		2729.5		24.19		24.715		14.99		0.395	U	67.15	
16940	D	1904.5		205		11.815		655		2671.5		25.545		26.25		15.3		0.3	U	64.65	
17705	D	2291.5		244.55		11.665		900		2865		19.9		24.055		17.045		0.795	J	86.9	
16885	D	2277		243.05		11.825		909.5		3011.5		21.015		24.085		16.69		0.73	J	85.75	
17720	D	2289.5		242.8		11.675		908.5		2708.5		18.31		23.59		16.36		0.62	J	75.5	
17955	D	2259		242.7		11.475		897		2870.5		20.03		24.005		16.71		0.84	J	92.9	
16750	D	2259		241.1		11.61		900		3030		21.19		23.81		16.76		0.63	J	73	
17584.1	D	2303.3		247.75		11.706		591.4		3020.9		21.432		24.452		16.958		0.975	J	84.94	
17360	D	2288.5		246.05		11.535		595		2878.5		20.04		23.755		16.515		0.79	J	73.65	
17200	D	2268		244.9		11.665		608.5		2865		20.165		23.725		16.275		0.83	J	84.8	
13965	D	1652.5		180.7		8.83		415.5		2163.5		18.78		17.265		13.43		0.415	J	52.35	
17525	D	2230.5		243.55		11.765		631		2983.5		21.64		22.83		15.515		0.685	J	83.45	
17225	D	2214		241.2		11.875		620		2907		21.005		23.785		15.805		0.665	J	76.3	
17435	D	2176		237.8		11.495		629.5		2919		22.18		22.965		15.31		0.585	J	73.35	
16400	D	2167.5		235.55		11.425		630.5		3131.5		23.265		24.08		15.655		0.635	J	73.1	
17200	D	2176.5		236.15		11.785		622.5		2751		19.355		24.065		15.425		0.89	J	106.8	

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14. ABSTRACT Research over the last decade has revealed that energetic constituents are released into the environment as a result of military training in extremely heterogeneous patterns. Traditional soil sampling and sample preparation methodologies are inadequate to address this level of heterogeneity. Consequently, a number of necessary changes to the accepted soil sampling and sample preparation procedures, which were adopted in a revised U.S. Environmental Protection Agency (USEPA) Method 8330B are identified. Recently, there have questions about whether the above questions also substantively apply to other constituents, such as metals, semi-volatile organic compounds, and polychlorinated biphenyls. Preliminary data suggest metal residues from small arms and pyrotechnic military training are heterogeneously distributed. As a result, regulatory agencies are increasingly requiring the DOD to apply USEPA Method 8330B to the sampling and processing of soils from small arms ranges containing metals. However, there is no published research indicating whether changes to USEPA Method 3050B for metals are needed or warranted. This study assessed USEPA Method 8330B and whether it is applicable to soils containing metals. The utility of multi-increment sampling versus traditional grab/discrete sampling was assessed and found to yield reproducible and more representative metals soil concentrations. In addition, changes to the soil digestion procedure, USEPA Method 3050B, were evaluated and included the following: 1) necessity of machining or grinding of the soil, appropriate type of grinding apparatus and grinding interval; 2) assessment of the need to increase the digested mass and digestion interval; 3) optimum soil to acid ratio, i.e., digestion efficiency; 4) sub-sampling to build the digestate sample; and 5) disposition of the oversize fraction, i.e., material larger than 2 mm.					
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